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PAPERS IN PRESS FOR FORTHCOMING ISSUES

San Andreas, Garlock, and Big Pine Faults, California. By Mason L. Hill and T. W. Dibblee, Jr.

Siliceous Sediments of Ouachita Facies in Oklahoma. By August Goldstein, Jr., and Thomas A. Hendricks.

Geology of the Chloride Quadrangle, Arizona. By Blakemore E. Thomas.

Tertiary Geology of the Galisteo-Tonque Area, New Mexico. By Charles E. Stearns.

Terminology for Stratification and Cross-Stratification in Sedimentary Rocks. By Edwin D. McKee and Gordon W. Weir.

Relation of Gravity Anomalies to the Geology of Central Vermont and New Hampshire. By Robert J. Bean.

Cenozoic Fill and Evaporite Solution in the Delaware Basin, Texas and New Mexico. By V. C. Maley and Roy M. Huffington.

Mudflow of 1941 at Wrightwood, Southern California. By Robert P. Sharp and Laurence H Nobles.

Pleistocene Geology of Part of Central South Dakota. By Dwight R. Crandell.

Systematic Drainage Changes in the Piedmont of North Carolina and Virginia. By William A. White.

BULLETIN OF THE GEOLOGICAL SOCIETY OF AMERICA
VOL. 64, PP. 255-258 MARCH 1953

REVIEWS OF GEOLOGIC LITERATURE: AN INNOVATION

Initiation of the Idea

At a meeting of the N. R. C. Division of Geology and Geography on April 29, 1950, it was suggested that a committee should look into "the feasibility of publishing summaries of geological research, important results, and outstanding contributions". A committee was appointed consisting of H. R. Aldrich, Perry Byerly, R. C. Moore, Franco Rasetti, W. W. Rubey, and E. Cloos as temporary chairman. The "Committee on Review Articles in Geology and Geography" accepted the task of formulating policies on the choice of fields and the organization and content of review articles, of obtaining the co-operation of competent leaders in various fields, and of arranging for publication. Invitations to submit review articles were sent to many potential authors, and, as papers began to arrive, the Committee was enlarged by the addition of Glenn Jepsen and Francis J. Pettijohn.

Objectives

This effort to publish comprehensive and timely discussions of interesting and important geological problems has the following objectives: (1) to help workers in each field of geology gain knowledge of the current advances and viewpoints in bordering sciences as well as in other branches of geologic science, (2) to screen voluminous literature and provide organized information and selected bibliographies of source materials in particular subjects, (3) to direct attention to favorable fields for additional studies and to stimulate their development, and (4) to provide a general reference and obviate the need for review sections in current papers within the specific field.

Scope

The range of subject matter is as broad as geology in its many ramifications, and in their union with physics, chemistry, biology, astronomy, and mathematics.

A good review article is a comprehensive summary of the literature bearing on specific subjects and embodies critical analysis and constructive synthesis of relevant data. Such a subject should not be an entire field, as petrology, or a whole subfield, as invertebrate paleontology. Nor should a review article stress many new discoveries or descriptions by the author.

Obviously, some of the "specific subjects" that are desirable choices for review articles may emphasize "comprehensive summary" rather than "critical analysis", and in other subjects the opposite may be true. For example, an informative and useful summary of the voluminous researches on coal balls, written primarily for the nonspecialist, could report many discoveries of paleobotanical and geological significance but largely omit elements of a technical critique. On the other hand, a review of the more meager literature on seismic surveys of the sea floor might advantageously consist much more largely of "critical analysis" than of "comprehensive summary".

In the judgment of the Committee, a type of "specific subject" that belongs in the domain of review articles may have geographic delimitation, as for example "geophysical exploration of the western Gulf Coastal Plain" or "structure of the Appalachian Piedmont". The aim of the review is a reasonably concise, authoritative summary, aimed primarily at organization of pertinent data, however widely scattered, providing perspective and making appropriate analyses in the light of present knowledge. An original paper of the same scope is primarily a report of the results of much new investigation and does not require the breadth and impartiality of a review.

Length of Articles

No restrictions on the length of a review article have been fixed. Reviews are not abstracts and hence are not limited to a fraction of a page or even a few pages. An essential aim

of the review, however, is to bring much into little. Limitation in reader time in relation to the tremendous volume of present-day geological literature is a compelling reason for undertaking the labor of writing review articles, and joined to this is the need continuously to take stock of advances in various fields.

Bibliography

Each review article should be accompanied by a bibliography of carefully selected references which cite most of the literature pertinent to the subject treated, so that an interested reader has the opportunity to go as far as he chooses into a possibly very comprehensive literature. Internal references to the bibliography should be to specific pages wherever possible. Bibliographic references should follow GSA practices.

Authors

The preparation of a review article is not only a responsible opportunity to advance the development of geology—it is also a very difficult task. A successful author must keep in mind the objectives of review articles and must be exhaustive in his coverage and thoroughly competent in his field. In order to initiate this series of geological reviews the Committee has invited authors of recognized eminence and skill to contribute the first articles.

Examples of Review Articles

The following are good examples of review articles, in the opinion of the Committee. They include some that are included in review journals such as *Review of Modern Physics*, *Biological Reviews of the Cambridge Philosophical Society, and Chemical Reviews*. They range within wide limits, depending on the journal and author, from brief essays based on only a few papers that are judged particularly important to sizable monographs that co-ordinate nearly all the literature on the subject. Some of these articles are terse summaries of individual contributions. Others—and these are often considered the best review articles—are critical appraisals that achieve a new synthesis of the pertinent literature on a specific subject. A few of these articles are truly original contributions to science in the strictest sense of the term.

It is much easier to find examples of comprehensive critical reviews in those fields of science that have established regular review journals. In geologic publications, reviews of the literature are commonly presented with a very different emphasis—to afford a background for some new observation or to cite evidence in support of some particular interpretation of the author. The geological articles cited herewith are more nearly of the true review type than is customary.

The three review articles which follow have been accepted to date out of the six or seven submitted. While they do not exhibit as great a number or as wide a range as hoped for, they have been advanced for printing in order that readers may get a better picture of goals set. The Committee hopes that these may stimulate production of others. Authors are invited to submit their manuscripts to the chairman of the Committee for regular handling through various stages of critical reading, recommendation, revision, and advancement toward publication.

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COMMITTEE ON REVIEW ARTICLES, DIVISION OF GEOLOGY AND GEOGRAPHY, NATIONAL RESEARCH COUNCIL.

BULLETIN OF THE GEOLOGICAL SOCIETY OF AMERICA
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METAMORPHISM OF BASALTIC ROCKS: A REVIEW

BY ARIE POLDERVAART

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INTRODUCTION

The influence of Read's thought-provoking series of papers (1939; 1943; 1944; 1946; 1948a; 1948b; 1949) dealing with problems of granite and metamorphism will probably still be felt many years hence. His two presidential addresses for the Geological Society of London (1948b; 1949) emphasize especially the space and time aspects of plutonism, the four-dimensional picture of metamorphic terrains. Metamorphic rocks are dead until made to tell of their past history, of earth history—that is, geology!

Throughout these meditations one is reminded time and again of the writings of that master student of the Finnish Precambrian tracts, Sederholm. Sederholm also wanted the rocks to come alive and yield the secrets of their past. However, he especially emphasized the unique role played by intrusions and lava flows of basaltic composition in the unravelling of the complicated history and space relations of metamorphic terrains, indeed called them the Ariadne thread which allowed him to view the rocks in their four-dimensional perspective (1923, p. 148). Read is less emphatic (1949, p. 131), but it is not entirely unexpected to see two of his former students (Sutton and Watson, 1951a) following Sederholm's Ariadne thread in the Precambrian of the Scottish northwest Highlands, nor to read of Read's enthusiastic approval that these authors "had now applied vast draughts of time to the dead rocks of the Lewisian" (1951, p. 297).

More recently the important role played by basaltic rocks in the understanding of the time-space aspects of metamorphism was again emphasized by Vuagnat (1951). This author finds that:

"Les roches basiques des Alpes ne sont pas très importantes au point de vue quantitatif.—Cependent ces roches moins fréquentes ont un intérêt particulier pour le géologue et le pétrologue tant par les problèmes qu'elles posent que par les renseignements qu'elles fournissent sur l'histoire de la chaîne alpine" (1951, p. 309).

It does not seem inappropriate, therefore, to review here some of the problems of basaltic rocks and metamorphism. During the last decade many new data have become available on the course of crystallization and the consolidation products of basaltic magma, both the undersaturated, oceanic, or olivine-basaltic type, and the saturated, or tholeiitic type. Most geologists still regard these rocks as truly eruptive, that is crystallized from a silicate melt (Shand, 1947)—in fact, the basaltic rocks are the solace of magmatists in these days of virulent transformism! One may derive comfort from the reflection that here at least are rocks which, to begin with, are of undisputed eruptive origin, of well-known and generally remarkably uniform chemical and mineralogical composition, and of familiar texture. Such comfort disappears soon enough after a contemplation of their metamorphic equivalents, here collectively called metabasaltic rocks.

Acknowledgments

The writer greatly appreciates the many suggestions and helpful criticism of Drs. W. H. Bucher, A. F. Buddington, and H. H. Hess, who read the manuscript.

Time and Metabasaltic Rocks

Sederholm found in the Finnish Precambrian terrain that a valuable time limit is given by basaltic dikes, which serve as fixed pointers on the geological time scale and, according to which rocks they cut and chilled against, or which rocks in turn cut the basic rocks, they determine what came before and what came after. Thus leptites of Svionian age in the Pellinge region (Sederholm, 1923) had been granitized and partly or wholly transformed into gray gneissic granite, prior to the intrusion of a swarm of diabase dikes. The dikes cut the leptites, granite gneiss, and migmatites, and the diabase is chilled against the older rocks. Later all these rocks were intruded and transformed by the red Hangö granite, which migmatized the older leptites and granite gneiss, intruded the basaltic dikes, and also encloses many altered relics of the earlier metadiabases. Sederholm remarked (1926, p. 31) that basaltic intrusions possess

> "a double interest, geologically and petrologically. On the one hand they give the criterion for separating the older and younger Archaean granites. On the other hand, they furnish a material on which the intensity of the metamorphic changes can be measured."

Waldmann (1927) applied the basic dike criterion to the Gföhl gneiss of the Waldviertel Moldanubicum and found the gneiss to be polymetamorphic, the two periods of metamorphism being separated by a phase of intrusion of basaltic dikes. A striking illustration of the use of this criterion was recently given by Sutton and Watson (1951a). In both the Loch Torridon and the Scourie area of the northwest Highlands of Scotland, these authors found evidence of three major episodes in the pre-Torridonian metamorphic history of the rocks: an older period of metamorphism (the Scourian epoch), a phase of diabase dike intrusion, and a younger period of metamorphism (the Laxfordian epoch). They write (p. 292) that

> "the metamorphic state of the dolerite dykes may be used to determine the age of the surrounding metamorphic complexes" while "uncertainty arises only where the dolerite dyke series is lacking"; they conclude that "the period of dolerite intrusion may therefore be taken as a fixed point in the history of the north-west Highlands."

The presence of diabase dikes in granite, chilled against the granite and yet intruded by the granite, appears at first sight an enigma. It is of such phenomena that Raguin remarks "fait paradoxal, ce granite est à la fois beaucoup plus vieux et beaucoup plus jeune que ce basalte" (1946, p. 19). Perrin and Roubault (1939; 1947) give several examples, while the present writer was privileged to see similar occurrences in southern Africa. The metabasaltic dikes in these cases yield the clue to the riddle of time and manner of granite formation; either the dikes originally intruded granite which was subsequently "rejuvenated" and mobilized to intrude the dikes in its turn, or the dikes originally intruded sediments which were later granitized, becoming sufficiently mobile to intrude the intrusions.

The Karroo diabases of the Union of South Africa (Walker and Poldervaart, 1949) yield perhaps the clearest examples of the process; they are only slightly different in that the diabases themselves are responsible for the formation of igneous-looking granophyres from pre-existing sediments, and diabases and granophyres are essentially penecontemporaneous. The Karroo basaltic magma intruded the associated sediments and chilled against them, yet later in the cooling history of the magma the sediments were mobilized and metasomatized to granophyres which cut the diabase and may even enclose more or less altered fragments of diabase. Similar phenomena are described by Kahma (1951) in the Satakunta diabase. In dealing with narrow metabasaltic dikes in plutonic regions the later granitization was probably not penecontemporaneous with the intrusion of basaltic magma, but essentially the same features are observed in the field.

However, relations are not always as simple as may appear at first sight. Fine-grained borders do not invariably mean chilled borders, but may instead mean recrystallized borders. Wells and Wooldridge (1931) studied gabbroidal xenoliths in granite from the island of Jersey.

The xenoliths are of three main types, according to whether they show (1) sharp margins without a decrease in grain size against the surrounding granite; or (2) sharp margins characterized by apparent "chilling", the gabbro becoming progressively finer grained when traced outward from the core; or finally (3) gradational contacts with the surrounding granite which are never marked by a decrease in grain size in the gabbro. The authors remark (p. 190) of the second type of xenoliths, that "the impression is conveyed that the xenoliths have been actually chilled against the invading magma, which is of course absurd".

Other authors have observed similar features along contacts of granite and metabasaltic rocks (Thomas and Campbell Smith, 1932; Taylor and Gamba, 1933; Joplin, 1935; Nockholds, 1935). The metagabbros of the Adirondacks show in many places fine-grained borders along contacts with the Younger granites, which fact caused Kemp and Alling (1925), Gillson, Callahan, and Millar (1928), and others to believe that the metagabbros are younger than these granites. Buddington (1939) proved the metagabbros older than the Younger granites and found that the apparently unequivocal evidence of fine-grained border facies is in some cases "wholly an illusion." The border facies have been recrystallized to a homogeneous granoblastic aggregate which may or may not be finer-grained than the central metagabbros. The textural differences between the recrystallized border facies and the central metagabbros account in many cases for the apparent finer grain of the former.

Thus there appear to be "pseudo" and actual fine-grained borders due to metamorphic recrystallization, and fine-grained borders due to actual chilling. Ariadne's thread is no longer so simple and can certainly not be followed out of the labyrinth without careful and detailed field and laboratory studies!

Palimpsest Structures, Relic Minerals, and Deformation

Sederholm (1926, p. 132) complained of rigid classification schemes of metamorphic rocks "giving place only to equilibrium types which are rather rare in nature". Read (1948b, p. 155) is even blunter and remarks of the facies classification of metamorphic rocks (Eskola, 1939):

> "the classificatory facies-concept, in that it deals with rocks considered to be equilibrium assemblages, is not of value in the determination of metamorphic history—non-equilibrium assemblages are much more important in that they allow the metamorphic history to be read."

Read (1949, p. 105) also condemns the notion that metamorphism is necessarily progressive in time, and states that

> "the preservation of original sedimentary textures—in the high-grade rocks of a so-called progressive series and their obliteration in the low-grade rocks—indicate that the observed series is not one of time; the high-grade rocks did not pass through the low-grade stage".

In distinguishing between pre-, para-, and post-crystalline deformation, Read (1949, p. 117) also loosened, though not entirely severed, the bond between deformation and metamorphism.

We may now enquire whether these statements also hold true for basaltic rocks, which in many ways especially favor such an enquiry. Diabases possess original textures which are easily distinguished from metamorphic textures. Many basalts are porphyritic or amygdaloidal, and the shapes of phenocrysts or amygdules may be a guide to the degree of deformation imposed upon the rocks. Moreover, the constituent minerals of basaltic rocks may serve as valuable pointers to the degree of metamorphic equilibrium attained. Original plagioclase may become clouded with slight metamorphism, but newly formed, recrystallized feldspar should not be clouded (MacGregor, 1931). If it is clouded, the rock may well be polymetamorphic. There are reasons to believe that MacGregor's interpretation of clouding of feldspars (exsolution of Fe contained in the original feldspar upon later reheating) is not entirely correct (*cf.* Grout, 1933; Reynolds, 1936; 1946; Anderson, 1937), but further work is necessary to establish the mechanism of thermally induced clouding of minerals. Original sodic plagioclase of diabases and basalts should belong to the high-temperature, volcanic series and can be distinguished optically from newly formed, metamorphic sodic plagioclase, which should belong to the low-temperature, plutonic series (van der Kaaden, 1951). The type and complexity of twinning in plagioclase

also indicates whether the crystals are original or recrystallized (Gorai, 1951). Rhombic pyroxenes of diabases and basalts, likewise, belong to a high-temperature, volcanic series, optically distinct from the low-temperature rhombic pyroxenes found in gabbroic and metamorphic rocks (Hess, 1952; Kuno and Nagashima, 1952). The augites of basaltic rocks fall along a particular crystallization trend with distinct optical properties (Poldervaart and Hess, 1951). Upon metamorphism and recrystallization the newly formed monoclinic pyroxenes should fall above this trend, and thus approach the compositions of members of the diopside-hedenbergite series. Palimpsest structures, relic minerals, and evidence of deformation should therefore be especially easily recognizable in metabasaltic rocks.

In turning to the literature, we may first note some examples concerning the rate and manner of response of basaltic rocks to metamorphic conditions. Sederholm (1923, p. 45) found it

> "an astonishing fact that we find here, among old Archaean basic rocks which usually have undergone such a complete metamorphism, rocks whose primary composition and texture have been so well preserved."

The younger metabasalts of the Pellinge group are much more altered than those of the Pernå formation, though the latter have been penetrated by granites before the eruption of the Pellinge metabasalts. The Pernå metabasalts may even show undeformed phenocrysts and amygdules. Sederholm (1923, p. 46) cautions that "metamorphic processes . . . cannot simply be regarded as a function of temperature and pressure" and urges that these facts be taken into account when using laboratory experiments to explain metamorphism. Buddington (1952) found metadiabases in the Adirondacks with relics of primary ophitic structure in which plagioclase had undergone a change in composition without any fundamental change in form.

It would be entertaining to list the authors who, with Sederholm, expressed surprise in finding primary textures and original minerals in apparently high-grade metamorphic, Archean, or other basaltic rocks. However, this would serve little purpose, except to confirm that metabasaltic rocks throughout the world have been tardy in responding to plutonic conditions, though both in the rate and manner of response they show puzzling differences among themselves, even in the same terrain and within short distances. Sutton and Watson (1951b), who recently discussed this question in some detail, found that the metamorphism of diabases can follow at least three alternative courses, in each of which relic minerals and structures can be recognized, and each of which is of regional type. They note (p. 32) that

> "although great variations in the course of metamorphism are to be found in different localities, they are all due to processes which fall within the broad division known as regional metamorphism, and it is to variations within this division, and not to such divergent phenomena as pure thermal or dislocation metamorphism, that they must be attributed".

Finally (p. 34) they arrive at the conclusion that

> "all regionally metamorphosed rocks cannot be regarded as members of a single series. It follows that no metamorphic rock can be looked on as abnormal or anomalous because it fails to conform to types shown to exist in another area."

Metabasaltic rocks may show so little response to changed conditions that the question often arises whether the rocks are part of the same cycle as the surrounding metamorphic terrain. Rogers and du Toit (1908, p. 41–43) likened an Archean metadiabase from Marydale, South Africa, to the late Triassic Karroo diabase in its unaltered appearance in the field and in thin sections. Cohen (1937) regarded the Baltimore gabbro, Maryland, as having been intruded before the metamorphism of the country rocks, but Herz (1951) states that the gabbro is younger than the metamorphic cycle.

It appears that the problem is not only why certain demonstrably pre-metamorphic basaltic rocks have undergone so little change, but also if little-changed basaltic rocks are pre- or post-metamorphic. If the field evidence is inconclusive, only detailed petrological and mineralogical studies of especially the border facies may provide the answer to the last question. Criteria which may be used in such studies have already been outlined.

Parallelism of minerals in metamorphic rocks, producing schistosity, foliation, or lineation, is

generally considered the result of deformation, and in many examples it has been possible to prove that this has been the case. At the same time it is also admitted that such parallelism may be due to mimetic crystallization along privileged planes, such as bedding in sediments (Read, 1949, p. 111). Basaltic rocks, of course, possess no bedding, and it is difficult to think of there being any privileged planes in these homogeneous, massive rocks. Hence it has been tacitly assumed that the planar or linear orientation in green schists and amphibolites is always due to para-metamorphic deformation. In most cases this cannot be denied, in others it becomes difficult to bring the assumed deformation in harmony with observed facts. Basaltic lavas of the green schist or amphibolite facies, showing perfect parallelism of chlorite or amphibole, may yet exhibit undeformed pillow structures or contain beautifully ellipsoidal amygdules (Sederholm, 1923). Dikes of granoblastic diabase in granite may have narrow borders of schistose amphibolite, yet even in the immediate vicinity of the borders, and even in the palimpsest structures and relic minerals, signs of stress in the metadiabase may be lacking. Vogt (1927) considered that diabase may be changed to green schist at high temperature without stress, while Hess (1933) found that the same change may be produced by hydrothermal action, likewise without stress.

Privileged planes for mimetic crystallization may have originated by differential expansion upon heating of cold rock. The parallelism of chlorite or amphibole may also be the result of growth parallel to the diffusion front, and at right angles to the direction of transfer of material. A third possibility is suggested by results obtained in the synthesis of micas and amphiboles in electromagnetic fields; parallelism may be determined by magnetic equipotential planes. Whatever the ultimate solution of this problem, it seems clear that parallelism of minerals, even in originally massive and homogeneous rocks, is not invariably the expression of deformational stress.

Metamorphic Grades and Facies

Having due regard for previous remarks concerning the fallacy of progressive metamorphism in terms of time, it will be attempted here to trace basaltic rocks in various intensities of metamorphism and, when possible, to correlate metamorphic intensities as observed in metabasaltic rocks with the metamorphic grades studied by Barrow (1893; 1912) and Tilley (1925; Elles and Tilley, 1930) in the pelites of the Grampian Highlands. Sutton and Watson (1951b) found that there are at least three possible lines of metamorphic evolution of basaltic rocks; it remains therefore to record them from examples given in the literature.

I. *"Normal" Trend of Metamorphic Evolution*

Wiseman (1934) studied the metamorphosed diabases of the central and southwest Highlands of Scotland. He found a normal metamorphic sequence in the metadiabases extending from the Argyll coast to Glen Clova, and the changes exhibited in the basaltic rocks could be correlated with those shown by the surrounding sediments. However, the metadiabases of Banffshire and Aberdeenshire showed changes which departed from the general scheme, while apparently they also did not conform with the metamorphic grade of the associated pelites. This last group of metadiabases Wiseman therefore considered to be "abnormal" and he did not study them in further detail.

In the normal metamorphic sequence of basaltic rocks Wiseman recognized three main stages:

(1) Chlorite and biotite zones of associated pelites. Metadiabases may preserve traces of original texture. Original minerals partly or wholly replaced by chlorite, pale-green hornblende, albite, and epidote.

(2) Garnet zone of associated pelites. Original texture of metadiabases generally destroyed. Oligoclase or andesine formed by reaction of albite and epidote. Chlorite either lacking or present only in minor amounts. Hornblende generally darker green than in previous stage. Local development of garnet.

(3) Sillimanite zone of associated pelites. Original texture destroyed. Hornblende partly or wholly replaced by pale-green diopsidic pyroxene, with or without some pleochroic hypersthene. Epidote either lacking or present in minor amounts. Garnet generally present.

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METAMORPHISM OF BASALTIC ROCKS: A REVIEW

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INTRODUCTION

The influence of Read's thought-provoking series of papers (1939; 1943; 1944; 1946; 1948a; 1948b; 1949) dealing with problems of granite and metamorphism will probably still be felt many years hence. His two presidential addresses for the Geological Society of London (1948b; 1949) emphasize especially the space and time aspects of plutonism, the four-dimensional picture of metamorphic terrains. Metamorphic rocks are dead until made to tell of their past history, of earth history—that is, geology!

Throughout these meditations one is reminded time and again of the writings of that master student of the Finnish Precambrian tracts, Sederholm. Sederholm also wanted the rocks to come alive and yield the secrets of their past. However, he especially emphasized the unique role played by intrusions and lava flows of basaltic composition in the unravelling of the complicated history and space relations of metamorphic terrains, indeed called them the Ariadne thread which allowed him to view the rocks in their four-dimensional perspective (1923, p. 148). Read is less emphatic (1949, p. 131), but it is not entirely unexpected to see two of his former students (Sutton and Watson, 1951a) following Sederholm's Ariadne thread in the Precambrian of the Scottish northwest Highlands, nor to read of Read's enthusiastic approval that these authors "had now applied vast draughts of time to the dead rocks of the Lewisian" (1951, p. 297).

More recently the important role played by basaltic rocks in the understanding of the time-space aspects of metamorphism was again emphasized by Vuagnat (1951). This author finds that:

"Les roches basiques des Alpes ne sont pas très importantes au point de vue quantitatif.—Cependent ces roches moins fréquentes ont un intérêt particulier pour le géologue et le pétrologue tant par les problèmes qu'elles posent que par les renseignements qu'elles fournissent sur l'histoire de la chaîne alpine" (1951, p. 309).

It does not seem inappropriate, therefore, to review here some of the problems of basaltic rocks and metamorphism. During the last decade many new data have become available on the course of crystallization and the consolidation products of basaltic magma, both the undersaturated, oceanic, or olivine-basaltic type, and the saturated, or tholeiitic type. Most geologists still regard these rocks as truly eruptive, that is crystallized from a silicate melt (Shand, 1947)—in fact, the basaltic rocks are the solace of magmatists in these days of virulent transformism! One may derive comfort from the reflection that here at least are rocks which, to begin with, are of undisputed eruptive origin, of well-known and generally remarkably uniform chemical and mineralogical composition, and of familiar texture. Such comfort disappears soon enough after a contemplation of their metamorphic equivalents, here collectively called metabasaltic rocks.

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The writer greatly appreciates the many suggestions and helpful criticism of Drs. W. H. Bucher, A. F. Buddington, and H. H. Hess, who read the manuscript.

TIME AND METABASALTIC ROCKS

Sederholm found in the Finnish Precambrian terrain that a valuable time limit is given by basaltic dikes, which serve as fixed pointers on the geological time scale and, according to which rocks they cut and chilled against, or which rocks in turn cut the basic rocks, they determine what came before and what came after. Thus leptites of Svionian age in the Pellinge region (Sederholm, 1923) had been granitized and partly or wholly transformed into gray gneissic granite, prior to the intrusion of a swarm of diabase dikes. The dikes cut the leptites, granite gneiss, and migmatites, and the diabase is chilled against the older rocks. Later all these rocks were intruded and transformed by the red Hangö granite, which migmatized the older leptites and granite gneiss, intruded the basaltic dikes, and also encloses many altered relics of the earlier metadiabases. Sederholm remarked (1926, p. 31) that basaltic intrusions possess

> "a double interest, geologically and petrologically. On the one hand they give the criterion for separating the older and younger Archaean granites. On the other hand, they furnish a material on which the intensity of the metamorphic changes can be measured."

Waldmann (1927) applied the basic dike criterion to the Gföhl gneiss of the Waldviertel Moldanubicum and found the gneiss to be polymetamorphic, the two periods of metamorphism being separated by a phase of intrusion of basaltic dikes. A striking illustration of the use of this criterion was recently given by Sutton and Watson (1951a). In both the Loch Torridon and the Scourie area of the northwest Highlands of Scotland, these authors found evidence of three major episodes in the pre-Torridonian metamorphic history of the rocks: an older period of metamorphism (the Scourian epoch), a phase of diabase dike intrusion, and a younger period of metamorphism (the Laxfordian epoch). They write (p. 292) that

> "the metamorphic state of the dolerite dykes may be used to determine the age of the surrounding metamorphic complexes" while "uncertainty arises only where the dolerite dyke series is lacking"; they conclude that "the period of dolerite intrusion may therefore be taken as a fixed point in the history of the north-west Highlands."

The presence of diabase dikes in granite, chilled against the granite and yet intruded by the granite, appears at first sight an enigma. It is of such phenomena that Raguin remarks "fait paradoxal, ce granite est à la fois beaucoup plus vieux et beaucoup plus jeune que ce basalte" (1946, p. 19). Perrin and Roubault (1939; 1947) give several examples, while the present writer was privileged to see similar occurrences in southern Africa. The metabasaltic dikes in these cases yield the clue to the riddle of time and manner of granite formation; either the dikes originally intruded granite which was subsequently "rejuvenated" and mobilized to intrude the dikes in its turn, or the dikes originally intruded sediments which were later granitized, becoming sufficiently mobile to intrude the intrusions.

The Karroo diabases of the Union of South Africa (Walker and Poldervaart, 1949) yield perhaps the clearest examples of the process; they are only slightly different in that the diabases themselves are responsible for the formation of igneous-looking granophyres from pre-existing sediments, and diabases and granophyres are essentially penecontemporaneous. The Karroo basaltic magma intruded the associated sediments and chilled against them, yet later in the cooling history of the magma the sediments were mobilized and metasomatized to granophyres which cut the diabase and may even enclose more or less altered fragments of diabase. Similar phenomena are described by Kahma (1951) in the Satakunta diabase. In dealing with narrow metabasaltic dikes in plutonic regions the later granitization was probably not penecontemporaneous with the intrusion of basaltic magma, but essentially the same features are observed in the field.

However, relations are not always as simple as may appear at first sight. Fine-grained borders do not invariably mean chilled borders, but may instead mean recrystallized borders. Wells and Wooldridge (1931) studied gabbroidal xenoliths in granite from the island of Jersey.

The xenoliths are of three main types, according to whether they show (1) sharp margins without a decrease in grain size against the surrounding granite; or (2) sharp margins characterized by apparent "chilling", the gabbro becoming progressively finer grained when traced outward from the core; or finally (3) gradational contacts with the surrounding granite which are never marked by a decrease in grain size in the gabbro. The authors remark (p. 190) of the second type of xenoliths, that "the impression is conveyed that the xenoliths have been actually chilled against the invading magma, which is of course absurd".

Other authors have observed similar features along contacts of granite and metabasaltic rocks (Thomas and Campbell Smith, 1932; Taylor and Gamba, 1933; Joplin, 1935; Nockholds, 1935). The metagabbros of the Adirondacks show in many places fine-grained borders along contacts with the Younger granites, which fact caused Kemp and Alling (1925), Gillson, Callahan, and Millar (1928), and others to believe that the metagabbros are younger than these granites. Buddington (1939) proved the metagabbros older than the Younger granites and found that the apparently unequivocal evidence of fine-grained border facies is in some cases "wholly an illusion." The border facies have been recrystallized to a homogeneous granoblastic aggregate which may or may not be finer-grained than the central metagabbros. The textural differences between the recrystallized border facies and the central metagabbros account in many cases for the apparent finer grain of the former.

Thus there appear to be "pseudo" and actual fine-grained borders due to metamorphic recrystallization, and fine-grained borders due to actual chilling. Ariadne's thread is no longer so simple and can certainly not be followed out of the labyrinth without careful and detailed field and laboratory studies!

Palimpsest Structures, Relic Minerals, and Deformation

Sederholm (1926, p. 132) complained of rigid classification schemes of metamorphic rocks "giving place only to equilibrium types which are rather rare in nature". Read (1948b, p. 155) is even blunter and remarks of the facies classification of metamorphic rocks (Eskola, 1939):

> "the classificatory facies-concept, in that it deals with rocks considered to be equilibrium assemblages, is not of value in the determination of metamorphic history—non-equilibrium assemblages are much more important in that they allow the metamorphic history to be read."

Read (1949, p. 105) also condemns the notion that metamorphism is necessarily progressive in time, and states that

> "the preservation of original sedimentary textures—in the high-grade rocks of a so-called progressive series and their obliteration in the low-grade rocks—indicate that the observed series is not one of time; the high-grade rocks did not pass through the low-grade stage".

In distinguishing between pre-, para-, and post-crystalline deformation, Read (1949, p. 117) also loosened, though not entirely severed, the bond between deformation and metamorphism.

We may now enquire whether these statements also hold true for basaltic rocks, which in many ways especially favor such an enquiry. Diabases possess original textures which are easily distinguished from metamorphic textures. Many basalts are porphyritic or amygdaloidal, and the shapes of phenocrysts or amygdules may be a guide to the degree of deformation imposed upon the rocks. Moreover, the constituent minerals of basaltic rocks may serve as valuable pointers to the degree of metamorphic equilibrium attained. Original plagioclase may become clouded with slight metamorphism, but newly formed, recrystallized feldspar should not be clouded (MacGregor, 1931). If it is clouded, the rock may well be polymetamorphic. There are reasons to believe that MacGregor's interpretation of clouding of feldspars (exsolution of Fe contained in the original feldspar upon later reheating) is not entirely correct (*cf.* Grout, 1933; Reynolds, 1936: 1946; Anderson, 1937), but further work is necessary to establish the mechanism of thermally induced clouding of minerals. Original sodic plagioclase of diabases and basalts should belong to the high-temperature, volcanic series and can be distinguished optically from newly formed, metamorphic sodic plagioclase, which should belong to the low-temperature, plutonic series (van der Kaaden, 1951). The type and complexity of twinning in plagioclase

also indicates whether the crystals are original or recrystallized (Gorai, 1951). Rhombic pyroxenes of diabases and basalts, likewise, belong to a high-temperature, volcanic series, optically distinct from the low-temperature rhombic pyroxenes found in gabbroic and metamorphic rocks (Hess, 1952; Kuno and Nagashima, 1952). The augites of basaltic rocks fall along a particular crystallization trend with distinct optical properties (Poldervaart and Hess, 1951). Upon metamorphism and recrystallization the newly formed monoclinic pyroxenes should fall above this trend, and thus approach the compositions of members of the diopside-hedenbergite series. Palimpsest structures, relic minerals, and evidence of deformation should therefore be especially easily recognizable in metabasaltic rocks.

In turning to the literature, we may first note some examples concerning the rate and manner of response of basaltic rocks to metamorphic conditions. Sederholm (1923, p. 45) found it

> "an astonishing fact that we find here, among old Archaean basic rocks which usually have undergone such a complete metamorphism, rocks whose primary composition and texture have been so well preserved."

The younger metabasalts of the Pellinge group are much more altered than those of the Pernå formation, though the latter have been penetrated by granites before the eruption of the Pellinge metabasalts. The Pernå metabasalts may even show undeformed phenocrysts and amygdules. Sederholm (1923, p. 46) cautions that "metamorphic processes . . . cannot simply be regarded as a function of temperature and pressure" and urges that these facts be taken into account when using laboratory experiments to explain metamorphism. Buddington (1952) found metadiabases in the Adirondacks with relics of primary ophitic structure in which plagioclase had undergone a change in composition without any fundamental change in form.

It would be entertaining to list the authors who, with Sederholm, expressed surprise in finding primary textures and original minerals in apparently high-grade metamorphic, Archean, or other basaltic rocks. However, this would serve little purpose, except to confirm that metabasaltic rocks throughout the world have been tardy in responding to plutonic conditions, though both in the rate and manner of response they show puzzling differences among themselves, even in the same terrain and within short distances. Sutton and Watson (1951b), who recently discussed this question in some detail, found that the metamorphism of diabases can follow at least three alternative courses, in each of which relic minerals and structures can be recognized, and each of which is of regional type. They note (p. 32) that

> "although great variations in the course of metamorphism are to be found in different localities, they are all due to processes which fall within the broad division known as regional metamorphism, and it is to variations within this division, and not to such divergent phenomena as pure thermal or dislocation metamorphism, that they must be attributed".

Finally (p. 34) they arrive at the conclusion that

> "all regionally metamorphosed rocks cannot be regarded as members of a single series. It follows that no metamorphic rock can be looked on as abnormal or anomalous because it fails to conform to types shown to exist in another area."

Metabasaltic rocks may show so little response to changed conditions that the question often arises whether the rocks are part of the same cycle as the surrounding metamorphic terrain. Rogers and du Toit (1908, p. 41–43) likened an Archean metadiabase from Marydale, South Africa, to the late Triassic Karroo diabase in its unaltered appearance in the field and in thin sections. Cohen (1937) regarded the Baltimore gabbro, Maryland, as having been intruded before the metamorphism of the country rocks, but Herz (1951) states that the gabbro is younger than the metamorphic cycle.

It appears that the problem is not only why certain demonstrably pre-metamorphic basaltic rocks have undergone so little change, but also if little-changed basaltic rocks are pre- or post-metamorphic. If the field evidence is inconclusive, only detailed petrological and mineralogical studies of especially the border facies may provide the answer to the last question. Criteria which may be used in such studies have already been outlined.

Parallelism of minerals in metamorphic rocks, producing schistosity, foliation, or lineation, is

generally considered the result of deformation, and in many examples it has been possible to prove that this has been the case. At the same time it is also admitted that such parallelism may be due to mimetic crystallization along privileged planes, such as bedding in sediments (Read, 1949, p. 111). Basaltic rocks, of course, possess no bedding, and it is difficult to think of there being any privileged planes in these homogeneous, massive rocks. Hence it has been tacitly assumed that the planar or linear orientation in green schists and amphibolites is always due to para-metamorphic deformation. In most cases this cannot be denied, in others it becomes difficult to bring the assumed deformation in harmony with observed facts. Basaltic lavas of the green schist or amphibolite facies, showing perfect parallelism of chlorite or amphibole, may yet exhibit undeformed pillow structures or contain beautifully ellipsoidal amygdules (Sederholm, 1923). Dikes of granoblastic diabase in granite may have narrow borders of schistose amphibolite, yet even in the immediate vicinity of the borders, and even in the palimpsest structures and relic minerals, signs of stress in the metadiabase may be lacking. Vogt (1927) considered that diabase may be changed to green schist at high temperature without stress, while Hess (1933) found that the same change may be produced by hydrothermal action, likewise without stress.

Privileged planes for mimetic crystallization may have originated by differential expansion upon heating of cold rock. The parallelism of chlorite or amphibole may also be the result of growth parallel to the diffusion front, and at right angles to the direction of transfer of material. A third possibility is suggested by results obtained in the synthesis of micas and amphiboles in electromagnetic fields; parallelism may be determined by magnetic equipotential planes. Whatever the ultimate solution of this problem, it seems clear that parallelism of minerals, even in originally massive and homogeneous rocks, is not invariably the expression of deformational stress.

Metamorphic Grades and Facies

Having due regard for previous remarks concerning the fallacy of progressive metamorphism in terms of time, it will be attempted here to trace basaltic rocks in various intensities of metamorphism and, when possible, to correlate metamorphic intensities as observed in metabasaltic rocks with the metamorphic grades studied by Barrow (1893; 1912) and Tilley (1925; Elles and Tilley, 1930) in the pelites of the Grampian Highlands. Sutton and Watson (1951b) found that there are at least three possible lines of metamorphic evolution of basaltic rocks; it remains therefore to record them from examples given in the literature.

I. *"Normal" Trend of Metamorphic Evolution*

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In the normal metamorphic sequence of basaltic rocks Wiseman recognized three main stages:

(1) Chlorite and biotite zones of associated pelites. Metadiabases may preserve traces of original texture. Original minerals partly or wholly replaced by chlorite, pale-green hornblende, albite, and epidote.

(2) Garnet zone of associated pelites. Original texture of metadiabases generally destroyed. Oligoclase or andesine formed by reaction of albite and epidote. Chlorite either lacking or present only in minor amounts. Hornblende generally darker green than in previous stage. Local development of garnet.

(3) Sillimanite zone of associated pelites. Original texture destroyed. Hornblende partly or wholly replaced by pale-green diopsidic pyroxene, with or without some pleochroic hypersthene. Epidote either lacking or present in minor amounts. Garnet generally present.

As a result of further work in other parts of the world Wiseman's "normal" scheme of metamorphism of basaltic rocks was slightly modified by Eskola (1939) and Turner (1948). The latter's correlation of critical mineral assemblages in metabasaltic rocks, Barrovian grades, and metamorphic facies is reproduced here in Table 1. Minerals that may or may not be present are given in parentheses.

TABLE 1.—MINERAL ASSEMBLAGES IN METABASALTIC ROCKS, METAMORPHIC FACIES, AND GRADES (Turner, 1948)

Mineral assemblage	Facies	Grade
Plagioclase-pyroxene (olivine)	Gabbro	
Plagioclase-hornblende (diopside) (garnet) (epidote)	Amphibolite	*Sillimanite*
		Kyanite
		Staurolite
Albite-hornblende-epidote (chlorite)	Epidote-amphibolite	*Almandine*
Albite-actinolite-epidote-chlorite *or* Albite-epidote-chlorite (calcite)	Green schist	*Biotite* *Chlorite*

Sugi's work on the Misaka series of Japan (1931) demonstrated that in the green schist facies two alternative mineral assemblages can be produced from the same initial basaltic rocks. Turner (1935) studied the effects of water and carbon dioxide on the metamorphism of basaltic rocks in the green schist facies and indicated the mineral assemblages formed with different controls (Table 2).

TABLE 2.—GREEN SCHIST FACIES CONTROLS (Turner, 1935)

Mineral assemblage	Control
Actinolite-albite-epidote-chlorite	CO_2 absent, H_2O insufficient to form chlorite from actinolite
Albite-epidote-chlorite-calcite	CO_2 present, H_2O sufficient
Albite-epidote-chlorite	CO_2 absent, H_2O sufficient
Albite-chlorite	CO_2 absent, H_2O abundant, removal of Al^{+3} and Ca^{+2}

Chlorite may survive even in the zone of almandine, while garnet does not necessarily appear at the almandine isograd (*cf.* Wiseman, 1934) and may be absent even in the sillimanite zone. Phillips (1930) suggested that the varying degree to which chlorite survives in higher metamorphic grades may be correlated with variations in the occurrence of garnet, but both chlorite and garnet may be lacking. Suzuki (1930) concluded that garnet in amphibolites does not necessarily imply higher metamorphic intensities, but may be due primarily to a suitable bulk composition.

II. *"Abnormal" Amphibolitic Trend of Metamorphic Evolution*

Wiseman's "abnormal" metadiabases were found by Sutton and Watson (1951b) to be the characteristic metamorphic phases throughout the northwest Highlands and Banff. The trend of metamorphic evolution of the "abnormal" rocks converges with that of the "normal" metadiabases in the amphibolite facies. It is therefore necessary to give here only the first four stages of the changes observed by these authors:

(1) Original texture preserved. Clouding of plagioclase; pyroxene and iron ore rimmed by dark bluish-green hornblende. Sporadic development of garnet.

(2) Original texture preserved. Pyroxene replaced by aggregates of pale-green hornblende and quartz. Ilmenite rimmed by sphene.

(3) Original texture modified. Recrystallization of clouded labradorite to equidimensional, clear andesine. Recrystallization of fine-grained hornblende-quartz aggregates to larger crystals.

(4) Complete destruction of original texture. Rock is an evenly grained amphibolite with

planar or linear orientation of hornblende, and consisting of plagioclase (oligoclase or andesine), quartz, olive-green hornblende, garnet, sphene, and little iron ore. Quartz inclusions in hornblende have almost entirely disappeared.

Both the change pyroxene–hornblende and the change plagioclase–oligoclase or andesine apparently occur at a metamorphic intensity below that of the garnet zone of the associated pelites, hence not in the amphibolite facies (Table 1). The trend of metamorphic evolution of basaltic rocks observed by Sutton and Watson appears to converge with the "normal" trend of Wiseman (1934), Eskola (1939), and Turner (1948) at their fourth stage in the amphibolite facies, or within the Barrovian almandine zone.

III. "*Abnormal*", *Granulitic Trend of Metamorphic Evolution*

The third trend of metamorphic evolution of basaltic rocks is characterized from the first by the presence of pyroxenes (Stillwell, 1918; Tilley, 1921; Temperley, 1938). The original augite becomes rimmed by small granules of pleochroic hypersthene and pale-green diopsidic pyroxene. Eventually all original augite is replaced by a granular aggregate of pleochroic rhombic- and pale-green diopsidic pyroxene. Hornblende may or may not be present; a dark-brown hornblende may be intermediate in the formation of the new pyroxenes, while a green hornblende is often later than the pyroxenes and may mark the waning phase of metamorphism. When recrystallization of plagioclase occurs, the new plagioclase may be more sodic, more calcic, or of the same composition as the original plagioclase. Garnet may be formed with high metamorphic intensities, and with its appearance the new plagioclase may become more sodic. Progressive granulitization of the rocks with increasing metamorphic intensities is often noted. Palimpsest textures and relic minerals are generally more conspicuous and persist to higher metamorphic grades than is observed in the other two trends of metamorphic evolution.

This third type of metamorphism of basaltic rocks is generally regarded as belonging to the granulite facies, often described as an "abnormal" metamorphic facies (Eskola, 1939), and generally considered characterized by "dry", very high temperature-pressure conditions (Eskola, 1939; Turner, 1948). The granulite facies is typical of many large plutonic tracts throughout the world (Ramberg, 1949) and can therefore hardly be considered an "abnormal" facies. Transitional facies between the granulite facies and the amphibolite facies have been described by Groves (1935), Sahama (1936), Nockolds (1940), and others. Poldervaart and von Backström (1949) found in the Kakamas area, South Africa, metabasaltic rocks of both the granulite facies and the amphibolite facies occurring within the almandine and sillimanite zones of the associated pelites, but in the biotite zone only amphibolites were encountered. Apparently the basaltic rocks here followed the same trend of metamorphic evolution as described by Sutton and Watson (1951b) throughout lower metamorphic intensities. With higher metamorphic grades the metadiabases fall essentially within the granulite facies, but near syntectonic granodiorite intrusions and their associated migmatites the metadiabases are within the amphibolite facies. Although the change from granulite to amphibolite facies is often ascribed to diaphthoresis, the evidence from the Kakamas area indicates that metadiabases of the granulite facies were not converted to amphibolites through retrograde metamorphism but that, depending on "dry" or "wet" conditions, either diabasic granulites or amphibolites were formed from the same initial basaltic rocks under the same metamorphic intensity. The metadiabases of the amphibolite facies may or may not contain garnet, even if the equivalent rocks of the granulite facies do contain garnet, but the garnet in the amphibolites is distinct from, and not a relic of, the garnet in the diabasic granulites. The latter rocks contain a deep-brown hornblende, the amphibolites a green hornblende, but this is not believed to imply a different metamorphic intensity, nor were relic brown hornblendes found in the amphibolites.

In this third trend of metamorphic evolution, rocks of basaltic composition frequently recrystallize to metabasalts of smaller grain size. This fact has also been emphasized in dealing with fine-grained border phases; they may represent either chilled or recrystallized modifications. In the Kakamas area the finest-

grained metabasalts occur in the localities of highest metamorphic grade (Poldervaart and von Backström, 1949). These observations contrast with the general tendency for the grain size of metamorphic rocks to increase with increasing grade (Verhoogen, 1948).

The role of water in metamorphism has recently been emphasized by Yoder (1952) in his study of the system MgO-Al_2O_3-SiO_2-H_2O. He found (p. 615) that, at about 600°C. and 15,000 psi, it is possible "to have assemblages suggestive of every one of the now-accepted metamorphic facies in stable equilibrium", and (p. 569) "the presence of an 'excess' or 'deficiency' of water vapor greatly influences the mineralogy of a metamorphic rock." He concludes that (p. 569) "the now-accepted critical assemblages which define the metamorphic facies *may* have formed under the same pressure and temperature conditions, the different facies being primarily a function of the bulk composition." Bulk composition therefore includes H_2O present in rocks, both before and during metamorphism.

Thus we find that basaltic rocks may follow at least three different trends of metamorphic evolution, often in the same terrain, and apparently even when originally the rocks were of the same composition. These different trends are of regional type and found the world over; they cannot therefore be regarded as "abnormal", nor are they nonequilibrium phases.

Eclogites and Glaucophane Schists

Eclogites and glaucophane schists are also of basaltic composition, and current views are that these rocks represent a special type of metamorphosed basaltic rocks. Some eclogites may be of magmatic origin (Eskola, 1939), but the most widely held opinion is that the change gabbro–eclogite was effected under very high temperature-pressure conditions, while the change gabbro–glaucophane schist resulted from high-pressure, low-temperature conditions (Eskola, 1921; 1939; Alderman, 1936). Metamorphic changes in basaltic rocks in relation to temperature and pressure are diagrammatically represented in Table 3.[1]

[1] The most recent representations of the P-T conditions for metamorphic facies are given by Rosenqvist (1952).

Fairbairn (1943) found that the packing index of glaucophane schist is 5.9, while that of eclogite is 6.2, against 5.4 for average diabase. He pointed out that the observed high degree of packing in these rocks is additional evidence favoring high pressure as the controlling factor in their formation. The similarity between eclogites and glaucophane schists was emphasized also by Washington (1901), Lacroix (1941), and Turner (1948). Amphibolitization of eclogites has been correlated with granite formation and migmatization (Alderman, 1936; Erdmansdörffer, 1938) and is also regarded as an example of retrogressive changes.

The above interpretations of the formation of eclogites, eclogitic amphibolites, and glaucophane schists have not remained unchallenged. Wagner (1928) considered that eclogites and basalts are not chemical equivalents. Several other authors also believe that eclogites and glaucophane schists may be formed from sedimentary rocks (*e.g.*, Wieseneder, 1932; Ghosh, 1941). The role of the original bulk composition in determining the mineral assemblages produced upon later metamorphism has been emphasized by several authors. Suzuki (1930) believed the many diverse metamorphic rock types of the Besshi series of Japan, which include eclogite and glaucophane schist, to be isophysical and attributed the profound facies differences exhibited solely to variations in the original composition of the rocks. Yoder (1952, p. 617) also thinks that eclogite, amphibolite, and green schist facies may be formed under the same temperature-pressure conditions. Wieseneder (1934) and Brière (1920) found eclogites associated with medium-grade schists in western France and the eastern Alps, respectively, and Wieseneder suggested that the limiting factor in the formation of eclogites is not depth, but a certain bulk composition. Alderman (1936) considered that the amount of albite present in the original rock, together with the composition of the original pyroxene, determines the formation of omphacite during metamorphism.

Korjinsky (1937) concluded from the absence of eclogites from Basement rocks that great depth was not a controlling factor in their formation. Backlund (1936) thought that the eclogitic amphibolites of Greenland were formed under high shearing stress and believed

that extreme dynamic pressure and high temperature may cause the formation of true eclogite. Kranck (1935) cited evidence indicating that eclogites were formed under directed stress. Dengo (1950) considered it reasonable to assume that the eclogitic and glaucophane amphibolites of Venezuela were formed at intermediate temperatures under directed pressure, and not at great depths.

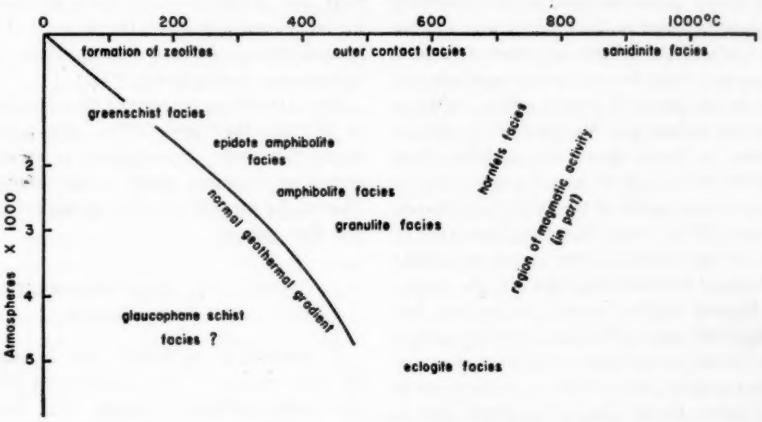
The role of solutions in the formation of eclogites and glaucophane schists was emphasized by such authors as Fiedler (1936), Hentschel (1937), Lacroix (1941), Taliaferro (1943), and Switzer (1945). Neither high pressure nor high temperature is thought to be necessary by some of these authors. Dengo (1950) made the valuable suggestion that the mineral assemblage of eclogite may be a metastable association formed as a step in the change of basaltic rock to amphibolite, in accordance with Ostwald's rule. Probably glaucophane schist similarly represents a lower metamorphic grade, perhaps the equivalent of the green schist or epidote amphibolite facies.

In his review of the eclogite problem Yoder (1950, p. 247) remarked:

> "It seems as though eclogite has been considered to be formed by all known major geological processes pertaining to igneous and metamorphic rocks."

This sums up admirably the present state of the problem.

TABLE 3.—MINERAL FACIES IN RELATION TO TEMPERATURE AND PRESSURE
(Barth, 1951)



THE ROLE OF GARNET

The role of garnet in metamorphism may be used to illustrate the apparently anomalous relations found in metamorphic rocks. Fermor (1913) found garnet so consistently associated with rocks interpreted to have recrystallized at depth that he called the mineral a geological barometer. Sederholm (1926) disagreed and pointed out that garnet is often found in partly granitized basic rocks. In the Enklinge area metabasaltic rocks show garnetiferous transitional phases next to granitized varieties. In the Kola Peninsula garnet amphibolites were probably formed when the rocks were granitized, and the migmatites are especially rich in garnet. Sederholm (1926, p. 127–128) remarked that

> "when grouping the minerals of . . . metamorphic rocks, it seems necessary to take into consideration not only the indications they give about temperature ('geological thermometers') and pressure ('geological barometers'), but also about the presence of water and other solvents (what may be called 'geological hygrometers')."

Buddington (1939, p. 187) described a granite-metagabbro contact from the northwest Adirondacks in which, approaching the granite, primary olivine, labradorite, and augite successively disappear in that order as recrystallization to hornblende, diopsidic pyroxene, hypersthene, garnet, and new plagioclase

progresses. This in turn is followed by the destruction of three of the newly formed minerals: first garnet, and next hypersthene and diopsidic pyroxene together. Thus there is an increase in the amount of garnet toward the contact, but at a point about a foot from the contact garnet disappears. However, at Gore Mountain, Levin (1950) found garnet in metagabbro becoming progressively larger as the contact with syenite is approached. Garnet here extends even beyond the contact, into the syenite-metagabbro hybrids. In the trend of metamorphic evolution studied by Sutton and Watson (1951b), garnet is present in the low-grade metadiabases, then disappears at a slightly higher grade, only to be encountered again in the amphibolite facies. Wiseman (1934) found that the appearance of garnet in the metadiabases of the southwest Highlands of Scotland coincides with the almandine isograd of the associated pelites, but Eskola (1939) concluded that in many cases it is impossible to correlate the presence of garnet in metabasaltic rocks with its occurrence in pelitic rocks. Bailey (1923) discovered that in the southwest Highlands the biotite zone is underlain by a metamorphic zone of two-fold type, characterized by either mica or albite, or mica and garnet, depending on a "wet" or a "dry" style of metamorphism. Yet Poldervaart and von Backström (1949) found in the Kakamas area that garnet may be present or absent in both "dry" or "wet" metamorphic equivalents of the basaltic rocks, although the associated pelites retained their garnet in the almandine zone, irrespective of the style of metamorphism. However, the garnets of the metabasaltic rocks have different physical constants, and therefore presumably also different compositions from those of the metamorphosed pelites.

The composition of garnet, its stability, the water-vapor pressure, and the relation between load and water vapor pressure all seem to play a part in determining whether garnet is formed during metamorphism. Yoder (1951) concluded that pyrope is not stable in the presence of "excess" water vapor in the temperature range investigated by him. He (1952, p. 623) also regards the appearance of garnet in metamorphism "as being dependent on the rate of growth and not on the attainment of a particular pressure and temperature." Garnets of eclogites are believed to be of a characteristoic composition, but analyses show a considerable range in composition, and garnets of many skarn rocks approach very closely the composition of eclogite garnet. Garnets rich in manganese appear to have a wider stability field and to be formed at lower metamorphic intensities and perhaps in the presence of higher concentrations of water than are those poor in manganese (Goldschmidt, 1921).

Hess (1952) has suggested that substitution of Al^{+3} for Mg^{+2} and Si^{+4} in orthopyroxenes should be further investigated as a potential means of assessing depth of crystallization. This might provide a better geological barometer than garnet.

Ortho- and Para-Amphibolites and Basic Fronts

It is of course well known that an amphibolite may represent a metamorphosed sediment or a metamorphosed basaltic rock, and that frequently it is extremely difficult to determine whether one is dealing with a para- or an ortho-amphibolite. Various criteria have been suggested to distinguish between the two types of amphibolites, but there still remain many border cases for which the origin has not been established. Palimpsest structures and relic minerals often allow for definite identification. The so-called "feather-amphibolites" (Adams, 1909) are usually of sedimentary origin. Sometimes contact-metamorphic borders are preserved, which establish the eruptive origin of the amphibolite. The range in composition, type, and complexity of plagioclase twinning may yield clues to the origin of the rock (Carlson, 1920). Finally, many ortho-amphibolites contain more Co, Ni, Cr, Sc, and Cu, and less Pb, Au, and Ba than para-amphibolites (Engel and Engel, 1951).

Rocks of different original bulk composition may converge during metamorphism in the production of amphibolites. Thus not only sediments of originally basic composition (calcareous shales, graywackes, or impure limestones) and basaltic rocks yield amphibolites upon metamorphism of the required intensity, but, according to some authors,

sedimentary and igneous rocks of different original composition may be changed through diffusion and metasomatism during metamorphism to yield identical or very similar amphibolites. This applies not only to amphibolites but to many metamorphic rocks of basic composition. Grout (1933; 1937) found that igneous-looking xenoliths of basaltic composition in the granite of the Giants Range and Boulder batholiths are transformed argillaceous rocks. Holmes and Reynolds (1947) even traced the transformation of quartzite into mica schist, induced by two intrusions of diabase, themselves altered to metadiabase and skarnlike rocks. Reynolds (1946) studied the compositional changes of granitization series and found that in the first stages rocks are frequently desilicated and either feldspathized, or basified, or both. Only during the more advanced stages are the rocks changed toward the composition of granite. Dennen's recent work (1951) on the baked contacts of small intrusions largely confirms Reynold's conclusions.

Basification of more acidic rocks during thermal metamorphism and the production of rocks of basaltic composition from them must apparently be accepted, but it is by no means generally believed that the same principles can be applied to regional metamorphism, in spite of Read's assertion (1939; 1948a) that regional metamorphism is thermal metamorphism on a regional scale.

The "basic front" concept applies the principle of initial basification of rocks to the field of regional metamorphism. In essence, it proposes that basic ions, such as Mg^{+2}, Fe^{+2}, and Ca^{+2}, advance through the crust ahead of the migmatite front and are accumulated in regions of low metamorphic grade to yield not only rocks rich in these constituents but even igneous-looking basic rocks (Wegmann, 1935; Anderson, 1937; Reynolds, 1944; 1946; 1947; Lapadu-Hargues, 1945; 1949). The production of amphibolites from calcareous sediments by skarnlike metasomatism is a less disturbing example of the operation of basic fronts, but even the presence of bodies of gabbro and ultrabasic rocks in the roof zones of large granite plutons has been pointed out as demonstrating basic fronts (Reynolds, 1944). This undermines the last stronghold of magmatists, but perhaps there is some consolation in the reflection that this interpretation may be rather too extreme, and may not withstand the test of time. Yet basification of pre-existing rocks by accumulation of Mg^{+2}, Fe^{+2}, and Ca^{+2} is a possibility which must be entertained seriously. Possibly original basaltic rocks of tholeiitic composition are thereby converted to amphibolites of olivine-basaltic composition, which would explain the preponderance of the last type of amphibolites in metamorphic terrains.

Whatever the final verdict on basic fronts, modern literature emphasizes migrations of material during granitization and metamorphism (Durand, 1950). It is not here of primary importance whether these migrations took place by diffusion in the solid, or whether they were vehicled by solutions. Probably both processes were active, and material was at the same time transported mechanically by solutions, ions diffused through fluids, and ions diffused through solids, depending on the size of the openings utilized (Holser, 1947). Of greater importance in the present connection is the weight of opinion favoring large-scale migrations of material during plutonic processes. It is believed that pre-existing rocks were thereby changed in composition, sometimes radically, sometimes but slightly. Throughout there is discernible in the literature a shift in emphasis from the viewpoint that metamorphic reconstitutions of rocks occur without significant compositional changes to one in which such reconstitutions are regarded as taking place in open systems.

This chapter might be concluded by reference to Buerger's pertinent remarks on metamorphism. Buerger and Washken (1947, p. 296) note that

> "the fact that something changes to something else in any kind of metamorphism shows that the new system has lower energy than the old."

They also find that a mineral does not recrystallize in the absence of solvents unless a certain "triggering" temperature is reached. This critical temperature is characteristic of the mineral and varies inversely with the degree of initial deformation. Finally, the fact that the activation energy of grain growth in metals is

about twice the activation energy required to make the metal atoms diffuse through their own solid structure (Beck, Kremer, and Demer, 1947) causes Buerger (1948, p. 114) to believe that in metamorphism

"whenever the temperature is sufficiently high to cause spontaneous growth of the crystals, it is already maintaining a very high level of diffusion."

Metamorphic Conditions

In the "normal" trend of metamorphic evolution, a basaltic rock is changed to a green schist with lower, and to an amphibolite with higher metamorphic intensities. The formation of both chlorite and of hornblende requires the addition of water to the original rock, but frequently this is also accompanied by other changes in composition. Most often it would seem that Al^{+3} and Na^{+1}, sometimes also K^{+1} and Si^{+4}, have been added to the rock, while Fe^{+2} and Mg^{+2}, sometimes also Ca^{+2}, have been removed in varying, but generally significant amounts. Changes in composition for the "normal" trend diabase—green schist or diabase—amphibolite are frequently more pronounced than for the "abnormal" trend diabase—diabase granulite. It appears to be customary to ignore these changes of composition which may accompany metamorphism, but the validity of this custom may be questioned. Eskola himself considered that the concept of metamorphic facies would be difficult to apply to open systems (1939, p. 344). Yet Ramberg (1949) adhered to the facies classification, although he emphasized the role of solid diffusion in metamorphism. Becke (1922, p. 227–228) believed that even in open systems there could be some sort of equilibrium. Thus, in the green schist facies, equilibrium would be reached when chlorite has been formed from all the available Mg-, Fe-, and Al-silicates in conformity with the governing temperature, pressure, water-vapor pressure, and concentrations of the various ions. As Read remarked (1948b, p. 176) this breaks down the ideal scheme of Eskola and necessitates the establishment of equilibrium in steps, as it were on a gradient of many qualities.

Both Eskola (1939) and Turner (1948) agree that the granulite facies is characterized throughout by "dry" metamorphic conditions. Nockolds (1937) also differentiated between mineral assemblages produced in rocks of the same composition under high temperature "dry", or low temperature "wet" conditions. Ramberg (1949, p. 34) considered that

"the water-vapor pressure in the pore system in rocks is usually higher in the granulite facies than in lower facies despite the smaller content of water in the granulite facies minerals."

Yoder (1951, p. 1493) found that

"several common hydrothermal alterations which have been interpreted as retrograde metamorphism, in the sense of lower grade, need not mean a change in pressure or temperature conditions, but may mean excess of water vapor."

Seemingly the problem is not whether the rocks contained water in their pore systems, but whether the minerals in the rocks reacted with the water present. The determining factors in this last relationship are not only temperature and external pressure, but also water-vapor pressure and concentrations of various ions participating in the different reactions. Walker and Poldervaart (1949) found that the relationship between load and water-vapor pressure determines largely whether or not the residual fluids of basaltic magma will interact with the associated rocks, while changes in composition of these rocks are determined primarily by the concentrations of the various ions present. It is not impossible that the same factors play a part in metamorphism. These considerations would seem to apply equally to so-called progressive metamorphism and to so-called retrograde metamorphism, and changes in mineral assemblages may be produced without corresponding changes in grade. Theoretically there is no reason why three or more trends of metamorphic evolution of basaltic rocks could not be produced from the same original rocks in the same terrain and under the same temperature-pressure conditions, provided there were differences in water-vapor pressure and ionic concentrations in different parts of the terrain, for instance caused by syn-metamorphic granitic intrusions. To regard these instances as "abnormal" or to ascribe them to diaphthoresis, without definite proof of abnormality or of retrograde metamorphism, would be to evade and confuse the issue.

It appears, then, that in many cases the approach to closed systems in metamorphism is near enough for equilibrium phases to be developed and for the application of the facies classification. However, in many other cases changes in bulk composition during metamorphism cannot be ignored, and indicate that metamorphic reconstitutions then take place in open systems, while temperature, pressure, and original composition are not the only factors that determine the mineral assemblages produced. Perhaps both schools of thought place too much emphasis on their version of metamorphic processes, without corresponding attempts to determine not only the original material, but also the exact manner in which this material was changed. Detailed studies of metamorphic minerals, relic minerals, and palimpsest structures appear to be more important in determining the origin and history of the rock than its classification according to one or other rigid system.

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FOSSILS IN METAMORPHIC ROCKS: A REVIEW

BY WALTER H. BUCHER

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INTRODUCTION

As one approaches a major orogenic belt from the undisturbed sediments of the foreland, one sees deformation increase progressively toward the metamorphic core. Low, open, nearly symmetrical folds change to high, asymmetric, and then to overturned folds. Shales with well-preserved fossils change to slates in which the cleavage cuts the bedding planes at all angles. Differential movement twists fossils out of shape, where they lie across the cleavage planes, and distorts them where bedding and cleavage coincide. In such cases it is possible to determine the greatest lengthening and shortening, if the original shape of the organic remains is sufficiently known, as was recognized long ago (Sharpe, 1847; 1849; Jannettaz, 1884). Some fossils tend to shear across when thus deformed, notably the belemnites, because of their radial-prismatic texture. This has happened even to belemnites embedded in soft clay shale where there has been strong differential shearing movement, as, *e.g.*, in the case of the common belemnites of the soft Cody shale (Cretaceous) where it has been sheared in the neighborhood of faults on the South Fork of the Shoshone River, about 25 miles above Cody, Wyoming. Corresponding changes are observed in limestones. In a classical study, Ernst Cloos has traced the progressive deformation of oölites across

the folded belt of Eastern Pennsylvania (Cloos, 1947, p. 843–918). Fossils share, of course, in the form change. The most extreme deformation of belemnites known to the writer was described from the Upper Jurassic limestone of the Fernigen syncline in the autochthonous Aare massif of the Northern Swiss Alps by Albert Heim (Heim, 1878, Atlas, pls. 14, 15; 1921, pl. 3, opp. p. 86).

Beyond the marginal zones of increasing mechanical deformation lies the regionally metamorphosed core of the orogenic belt. As one crosses the border, limestones are transformed into coarse-grained white marbles, and argillaceous rocks change from shales and slates into phyllites, mica schists, and gneisses. Instinctively the mind projects into the metamorphic core the progressive increase in mechanical deformation one observes on approaching its border. If mere mechanical deformation can accomplish so much distortion outside the metamorphic core—one is apt to reason—how much greater must be the internal reorganization within it! One thinks of "stress minerals" and subconsciously links stress with "distress", the all-pervading deformational changes that go on in a substance subjected to thorough kneading ("quälen", *i.e.*, torturing) and mashing ("quetschen"). One does not expect fossils to survive such imagined stress effects. No wonder a class of graduate students, coming from many schools, always breaks out in laughter when the suggestion is made that they look for fossils in metamorphic rocks.

Most geologists know that fossils have been found in metamorphic terrane, and many have seen an occurrence or two in the field. Yet, one does not speak of such specimens, as if they were freaks and perhaps embarrassing. Their existence is mentioned in contemporary treatises on metamorphism. They are said to be useful for determining the amount of distortion suffered by the rock in which they lie. But nothing is said about how great this amount is. No illustrations are given; the word "fossil" does not appear in the index of the treatises known to the writer (with one exception); and there are (practically) no references to the literature. This review aims to fill the gap. For, far from being useless curiosities, fossils in metamorphic rocks are documents of first importance to the understanding of metamorphism. They were recognized as such from the beginning (Daubrée, 1879, p. 138–144). They constitute still the most direct proof that highly crystalline rocks have formed from normal sediments (Grubenmann and Niggli, 1924, p. 62). Moreover, many show so little distortion in rocks ranging up to the highest grades of regional metamorphism that they challenge the instinctive reasoning set forth at the beginning of this Introduction. In the light of the facts, we may have to re-examine some ideas concerning regional metamorphism and the nature of the deformation within the metamorphic cores of orogenic belts.

Acknowledgments

The writer wishes to thank all those who helped him in the gathering of data, especially W. N. Cady (Vermont); Marshall Kay (Halobia in the Yerington District); T. Kobayashi (all references on Japan); T. S. Lovering (Michigan, Newfoundland); P. Niggli (more recent references concerning the Bündner Schiefer); J. B. Reeside (Cuba, Sierra Nevada); W. W. Rubey (the discovery of belemnites, as told by Clarence King); A. I. Stose (Pennsylvania, Virginia). The writer is also grateful to Charles Doll for sending specimens and data. Marland Billings kindly showed the writer the Massachusetts specimens he described and discussed them and additional recent finds with him. Finally, the writer owes special thanks to Arie Poldervaart for many helpful discussions and references on metamorphism, and for critical reading of the paper; and to Miss Amy L. Hepburn, the Department's chief librarian, for efficient and ever-patient help.

Fossils in the Liassic Bündner Schiefer of the Swiss Alps

Historical

In 1814, De Charpentier and Ch. Lardy found belemnites in mica schists on the Nufenen Pass in the Swiss Alps beneath towering heights of gneiss and granite (Lardy, 1832, p. 92). Other geologists soon verified the discovery. Élie de Beaumont visited the type locality and wrote about it to De la Bêche, who quoted in 1829 from the letter in his *Sketch of a classification of the European rocks* in the Philosoph-

ical Magazine. The letter tells of belemnites found in "an alternation many times repeated of small beds" of dark limestone and argillaceous schist "thickly studded with crystals of garnets and staurotides." The belemnites are "transformed into white calcareous spar, but ... the general forms and alveoli are nevertheless very visible, and can leave no doubt as to the nature of the fossils." These beds lie in a synclinal belt which northeastward passes into unmetamorphosed sediments. De la Bêche comments:

> "When such important changes ... can be fairly traced, what may we not expect to find in the sequel, when geologists shall cease to be contented with referring a particular mineralogical structure to the old divisions transition and primitive, of which the former seems only to have been created as a geological trap." (De la Bêche, 1829, p. 447–448).

In the first volume of his *Kosmos*, published in 1845, Alexander von Humboldt quotes the Nufenen belemnites as among the most conspicuous proofs of the transformation of rocks "through plutonic influence." He also mentions belemnites which De Charpentier had collected on the west side of the Col de Seigne, a pass east of Mont Blanc, and shown him in 1822. The limestone, which belongs to the same structural belt as the rocks on Nufenen Pass, 85 miles (135 km.) to the northeast, had until then been considered as of primordial age (Von Humboldt, 1845, quoted from reprint of 1874, p. 166 and p. 290). The belemnites of this Alpine belt of schists are, thus, the earliest known and the most widely reported fossils from metamorphic rocks. They played an important part, in the early days of geology, in turning in the right direction geologic thought concerning the nature of metamorphic rocks.

Rocks and Fossils

The fossiliferous metamorphic phase lies in a conspicuous synclinal belt of *Bündner Schiefer* that runs from the south side of the Gotthard massif southwestward along the longitudinal valleys of the Upper Rhine and Rhone rivers to the Mont Blanc region where it swings southward, following the bend in the Alpine chain.[1]

The famous fossil localities lie east-northeast and west-southwest of the mouth of the St. Gotthard Tunnel (Airolo)—*e.g.*, the Nufenen Pass which leads from the headwaters of the Rhone into those of the Ticino River; the Lukmanier Pass which connects a southern branch of the headwaters of the Rhine with a tributary of the Ticino; and the small Val Piora and Mt. Scopi near by.

Where not metamorphosed, the Liassic *Bündner Schiefer* are dominantly black shales and slates. They are generally more or less calcareous, though wholly noncalcareous zones are not rare. In addition, they include a wide range of minor intercalations which range from highly calcareous shales to layers of pure limestone, and from sands and "echinoderm breccias" (chiefly crinoidal) to sandstones. The metamorphic equivalents of these sediments constitute, accordingly, a highly diversified series among which black satiny phyllites and schists, rich in graphitoid, predominate. Among the other rock types may be mentioned white crystalline marbles; micaceous calcareous phyllites with occasional layers rich in echinoderm fragments, quartz, and muscovite; calcareous phyllites with zoisite, chloritoid, plagioclase, and crinoid stem joints, belemnites, pelecypods, and impressions of ammonite shells; muscovite schists rich in phenocrysts of garnet (almandine), zoisite, and belemnites; muscovite-biotite schists with cyanite, zoisite, epidote, and staurolite; quartz-mica schists with garnet, actinolite, staurolite, cyanite, epidote, zoisite, plagioclase, tourmaline, etc.; and even albite-biotite gneisses (Heim, 1891a, p. 260–267; Schmidt, 1891, p. 39–72; Heim, 1922, p. 496; Eichenberger, 1924, p. 451; Bossard, 1929, p. 128–158; Niggli, 1929, 166–170).

By tracing along the strike, the transition from the unmetamorphosed sediments into their highly crystalline equivalents can be followed step by step. The degree of metamorphism rises as one goes horizontally from the widest parts of the belt to the narrowest—that is, the most compressed part (Heim, 1891a,

[1] For an overall picture of the zone and location of famous localities, the following maps are probably most readily available to American readers: The sheets Sion (№ 6) and Ticino (№ 7) of the beautiful *Geologische Generalkarte der Schweiz*, 1:200,000 (Buxtorf and Christ, 1942). Staub's *Geologische Wandkarte der Schweiz* is drawn in the same scale, without topography. See also the tectonic map of the Swiss Alps in Heim, 1922, pl. 26, opp. p. 544, or the older geologic map of Switzerland, 1:500,000 (Heim and Schmidt, 1911).

p. 252), and, also, as one goes down vertically from the highest peaks into the lowest exposures in the valleys (Heim, 1891a, p. 266). In fact, observations in the *Bündner Schiefer* belt led Albert Heim to recognize first the possibility, then the reality, of metamorphic transformation of sediments without any recognizable relation to magmatic intrusions (Heim, 1891a, p. 252).

It is this character of the belt that gives importance to the occurrences of fossils in it. They seem so strangely out of place. Specimens of a garnet-zoisite-mica schist containing belemnites which Heim demonstrated at the International Geological Congress in London in 1888 (Heim, 1891b, p. 80–85), caused T. G. Bonney to write (1890, p. 213–214):

"... in one or two cases (they) certainly bore a strong resemblance to the black garnet schist described above. Still I was not quite satisfied of the identity of the rocks, and some scepticism seemed more than justifiable, for it was very difficult to understand how such a fossil as a belemnite could have retained its characteristic form while molecular changes of such importance were taking place in the matrix of the rock.... The more I considered the question,... the greater appeared the difficulties involved in the hypothesis, the stronger the possibility of some mistake."

So Bonney went back to the *Bündner Schiefer* belt about which he had written earlier (Bonney, 1886) and tried hard to prove that the beds with the fossils were not really crystalline schists[2] and could be distinguished from the latter which he took to be older. Limiting himself to the examination of a few transverse sections, he ascribed to the "true" (and hence "older") crystallines certain marbles and high-grade schists which, when followed along the strike, turn out to be inseparable parts of one and the same continuous belt of *Bündner Schiefer* (Heim, 1891a, p. 318–319).

The belemnites, which are quite common in some zones, are at many places little deformed. In occasional specimens, both the alveole and the pointed end are present, so that at least the most common form can be specifically identified as that of a typical Liassic species (*B. paxillosus* Schlotheim). The original radial and concentric texture, so characteristic of belemnites, is clearly visible on weathered specimens, although the microscope shows only a mosaic of calcite crystals. Here and there, even at the best localities, individual belemnites are bent or broken. In some zones they have been

[2] Bonney made much of the observation that the particular beds with belemnites that he had seen did not contain garnet, but "dirty hydrous minerals" that turned out to be zoisite. This insistence on a mineralogical detail which he thought to be diagnostic of a difference in age caused much confusion among English readers. The story is told by E. B. Bailey in his delightful *Tectonic essays* (1935, p. 108–111).

PLATE 1.—FOSSILS IN REGIONALLY METAMORPHOSED ROCKS

FIGURE 1. Impression of an ammonite (*Arietites*), 4.7 inches long, in fine-grained zoisite-biotite schist. Bündner Schiefer, Nufenen Pass, Switzerland. (Salomon, 1911, Pl. 9, fig. 1).

FIGURE 2. Sections of *Gryphaea* in greenish-gray marble layer. Bündner Schiefer, Val Lugnetz, Switzerland. (Heim, 1891a, Pl. 5, fig. 3).

FIGURE 3. Section of *Cardinia* in zoisite-garnet-micaschist. Bündner Schiefer, southwestern slope of Mt. Scopi, Switzerland. (Heim, 1891a, Pl. 5, fig. 8).

FIGURE 4. Sections of stem joints of *Pentacrinus*, in layers of micaceous, schistose limestone. Bündner Schiefer, Val Medel (large) and Val Rondadura (small), Switzerland. (Heim, 1891a, Pl. 5, figs. 9, 10).

FIGURE 5. Impression of *Spirifer* (?) in schistose quartz-plagioclase-garnet-biotite gneiss, Mt. Clough, New Hampshire. Greatest length of the fossil shown is about 1 inch. (Billings and Cleaves, 1935, p. 532, Fig. 2).

FIGURE 6. Impression of a *Spirifer* in what once was the inner part of a concretion, and now consists of quartz, clinozoisite, diopside, actinolite and titanite. The concretion lies in a quartz-biotite-andesite-garnet schist. Left side of shell, showing distinct ribs, is ½ inch long. (Billings and Cleaves, 1935, p. 531, Fig. 1).

FIGURE 7. Impression of *Spirifer murchisoni* in quartz-muscovite-biotite schist, with lesser amounts of orthoclase, oligoclase, zircon, and a few crystals of sillimanite. Greatest length of visible part of shell about 2.3 inches. South Strafford, Vermont. (Doll, 1943, Pl. 1, fig. 1).

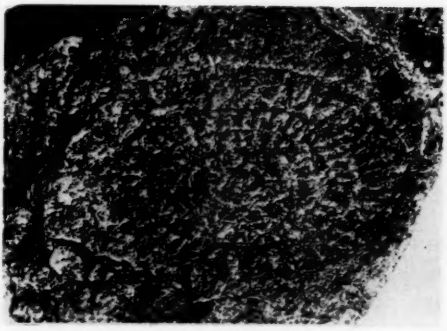

FIGURE 1

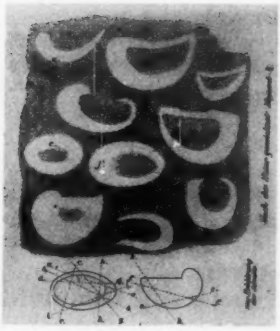

FIGURE 2

FIGURE 3

FIGURE 4

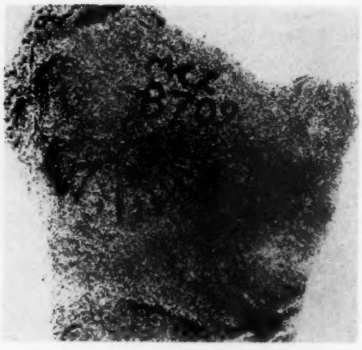

FIGURE 5

FIGURE 6

FIGURE 7

FOSSILS IN REGIONALLY METAMORPHOSED ROCKS

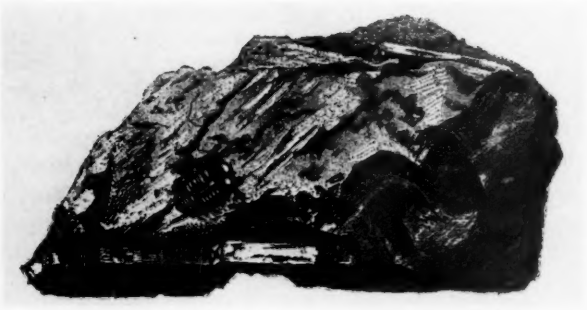

FIGURE 1

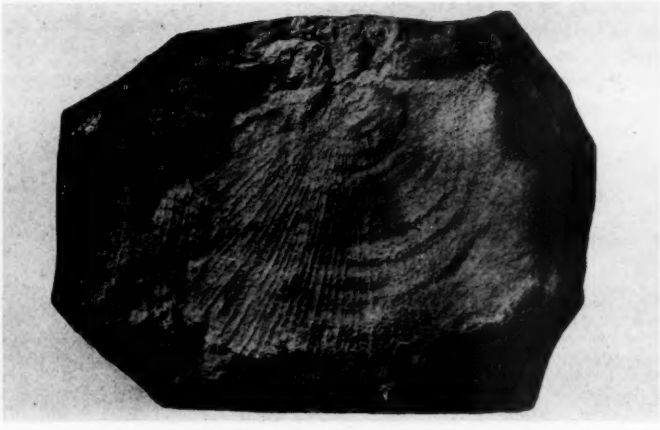

FIGURE 2

FIGURE 3

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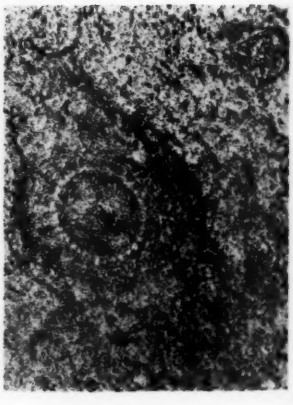

FIGURE 5

FOSSILS IN CONTACT-METAMORPHIC ROCKS

strongly deformed, torn apart, or squeezed and eventually reduced to irregular calcareous blebs in the schist, the nature of which could not be recognized or even suspected, if all transitional steps between the original and the final product were not available. How much of such deformation is due to later orogenic epochs that followed after the metamorphism had been achieved is not clear from the literature.

The significant fact is that, at a number of places and in different zones of the *Bündner Schiefer* belt, metamorphism has advanced to the garnet-zoisite-mica facies without causing the sort of form changes in the enclosed belemnites that are frequently seen in sediments strongly deformed by movements on discrete shear planes or by strong stretching and shortening.

Heim ascribed this preservation of belemnites to their solid nature. "Less solid fossils have been made wholly unrecognizable by mashing . . ." ("Quetschung") (Heim, 1891a, p. 303). This was, after all, consistent with the instinctive view with which this discussion opened. But here, as so often, the instinct was wrong.

On a memorable August day in 1907, under the unforgettable guidance of Professor Wilhelm Salomon, the writer had the exciting experience of collecting hazelnut-sized specimens of garnets in glistening mica schist near Airolo and then seeing the belemnites in the dark-green garnet-zoisite-biotite schist of the same belt on the Nufenen Pass.

On that occasion the impression of an ammonite (*Arietites*), 8 cm. wide and 12 cm. long, was found which was later described by Salomon (1911, p. 220–224). (One of his photographs is here reproduced as Figure 1 of Plate 1.) The shell is deformed, having been stretched by almost one fourth of the original diameter in one direction and shortened at right angles to it by a similar amount. This is relatively mild deformation. The good preservation of the radial ribs on the impression of the shell shows that, while there has been a general inelastic form change, there has been no internal granulation ("mashing") nor significant shear move ment in the rock.

The fact that the impression of a shell should have survived recrystallization seemed most surprising. The shell impression, like innumerable other partings in the rock, is coated with a reddish-brown film of limonite. Salomon assumed that in the original rock the shell had been replaced by pyrite whose presence made possible the preservation of the shell and of which weathering had left only the rusty coating on the impression. He found himself compelled to make this assumption (although no pyritized shells are recorded from the unmetamorphosed *Bündner* shales), because he found it difficult to believe that a mere impression could survive recrystallization.

That internal "mashing" or movements on closely spaced shear planes were lacking during the recrystallization, at least in some zones, is shown by the astonishing preservation of pen-

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PLATE 2.—FOSSILS IN CONTACT-METAMORPHIC ROCKS

FIGURE 1. Specimen of Ordovician shale (Schiste d'Angers) with trilobite (*Calymene*) and two crystals of andalusite (chiastolite). The crystal near the base is 7½ inches long. Sainte-Brigitte near the Salles de Rohan, Brittany (Lacroix, 1893, p. 45, Fig. 23).

FIGURE 2. Impression of *Halobia* in solid garnet rock (half way between grossularite and andradite). Triassic. Near McConnell mine, Yerington Mining District, Nevada (Knopf, 1918, Pl. 2, fig. A).

FIGURE 3. Thin section of a lime-silicate layer in which fossil remains are replaced by diopside and epidote. Devonian. Near Bonne-Fontaine, southeast of Grande Fosse, Alsace (Vosges). Original enlarged 60 times. (Largest oval section is 0.15 mm. long). (Jérémine, 1933, Pl. 2, fig. 1).

FIGURE 4. Thin section of a lime-silicate layer, showing echinoderm texture surrounded by diopside. (Original enlarged 70 times). Devonian. Near Bonne-Fontaine, southeast of Grande Fosse, Alsace (Vosges). (Jérémine, 1933, Pl. 2, fig. 2).

FIGURE 5. Siliceous shale with radiolarian skeletons. The interior of each skeleton is filled with biotite, muscovite, and albite. Note halo of mica surrounding each skeleton. Devonian. Above Moyenmoutier, Alsace. (Vosges). (Jérémine, 1933, Pl. 1, fig. 3).

tagonal crinoid stems at a number of places in the classical region. They occur in highly micaceous, schistose limestone layers. Illustrations of two such specimens from Heim (1891a, Atlas, Pl. V, Fig. 9, 10) are here reproduced as Figure 4 of Plate 1. The larger stem joints show the characteristic cross-section of *Pentacrinus tuberculatus* (Heim, 1891a, p. 306–307). In some cases, the spongelike ("cribriform") texture characteristic of echinoderms is still seen, in thin section, preserved as a relict texture in the interior of echinoderm fragments, while it has disappeared from the outer zones. In a few cases, elements of the echinoderm texture have been replaced by magnetite and even by zoisite (Schmidt, 1891, p. 42), proving beyond all doubt that metasomatic replacement in these rocks is quite independent of any mechanical destruction of textural elements.

Cross sections of coarsely recrystallized pelecypod shells, seen occasionally in the metamorphic zones of the *Bündner Schiefer*, tell the same story, such as that of a thick-shelled *Cardinia* in a calcareous zoisite-mica schist (Heim, 1891a, Atlas, Pl. V, Fig. 8, here reproduced as Figure 3 of Plate 1) and, in a greenish-gray crystalline marble rich in small grains of magnetite, numerous cross sections of a *Gryphaea* (shown on Pl. 1, fig. 2, reproduced from Heim, 1891a, Pl. V, Fig. 3). The line sketch below the figures of the *Gryphaea* sections shows that the variable shell outlines are merely the shapes of chance sections cut in different directions through the strongly curved, thick shell of *Gryphaea cymbium*, a common Middle Liassic species. These specimens show practically no distortion.

Schmidt's petrographic descriptions of the rocks in question bring out sharply the high degree of recrystallization (Schmidt, 1891), p. 39–72). Only a few telling details may be mentioned here. (a) Chloritoid porphyroblasts abound in black, graphitoid-rich, thin-platy phyllites and schists of which the groundmass consists of quartz, plagioclase, and sericite, with epidote or zoisite, rutile, and tourmaline as accessory minerals. Even where the groundmass is very fine-grained and the rock seems to lack schistosity (the so-called "hornfels")[3], the microscope reveals a well-defined microscopic parallel texture. This microscopic foliation passes interruptedly right through large porphyroblasts of garnet, zoisite, and a green mica (meroxenite) (Schmidt, 1891, Pl. 8, Fig. 6, 8). (b) Porphyroblasts of cyanite occur in graphite-free, more or less quartz-rich mica schists. (c) Muscovite schists full of porphyroblasts of mica and staurolite are less common, but locally well developed, and so on.

The complexity of the rock types becomes still greater at the base of the *Bündner Schiefer*, where iron-rich zones, impure dolomites, and quartzites appear. Detailed petrographic descriptions of the whole complex are given by Bossard (1929), and Niggli (1929) has discussed the chemical petrology with the aid of numerous analyses. Niggli concludes that the multitude of rock types represents essentially an "isophysical rock series," which owes its metamorphic character to the "dislocation metamorphosis of highest degree" produced by squeezing between the central massif and the Pennine *decken* (Niggli, 1929, p. 186), bearing out the conclusion which Heim had reached more than 40 years earlier. In the midst of these rocks lie the fossils!

Fossils in the Silurian and Devonian of New England

Massachusetts

In North America, fossils have been known in metamorphosed rocks at least since 1835. In that year, in the second edition of his *Report on the geology, mineralogy, botany, and zoology of Massachusetts*, Edward Hitchcock reported as follows (p. 295):

> "Since the first edition of the first part of my Report was published, I have had the satisfaction of discovering organic remains of the family of encrinites, in the bed of limestone in Bernardston. From the highly crystalline character of most of this rock, I had been led to suppose it older than the encrinal or transition limestone; and that it formed a bed in the slate of Bernardston, which appears to be one of the oldest varieties of that rock. But [he unfortunately concluded], its organic remains settle the question of its position."

Since, according to current doctrine, crinoidal limestone did not belong in the company of highly crystalline rocks, he explained away what he saw by assuming that this limestone must lie "beneath the oldest variety of the new

[3] Bossard (1929, p. 126) suggests that the high content in graphitoid has had a retarding influence on crystallization which might account for some of the peculiarities of these rocks.

red sandstone series . . . and upon the argillaceous slate, in an unconformable position." He was sufficiently impressed, however, to include a figure of a specimen on Plate XIV of the Atlas.

Some fifty years later, B. K. Emerson studied the Bernardston locality in considerable detail and proved that the fossil-bearing limestone is part of a conformable series; that the fauna of the lower limestone, with large crinoids and corals, is different from that in the upper limestone where the crinoids are small and "annulate", and brachiopods (especially spirifers[4]), gastropods and pelecypods prevail; and finally, that this same higher fauna extends into the overlying calcareous sandstone (Emerson, 1890).

Another 50-odd years after Emerson's work, Balk mapped "the entire outcrop area of the metamorphosed but fossiliferous Bernardston formation" under the auspices of the U. S. Geological Survey. His findings, reported so far only in a brief abstract, confirm Emerson's observations. According to Balk, a "lens of impure, partly mineralized, fossiliferous marble; quartz-conglomerate lenses; and lenticular bodies of metatuff (?), rhyolite, amphibolite, and metadiabase" are interbedded in a succession of argillaceous phyllites, in that (ascending) order (Balk, 1941, p. 2009).

How well metamorphosed the series is in which this limestone occurs may be seen from Emerson's description. It consists of an intensely crumpled phyllitic sequence ("the argillite") below; a quartzitic, partly conglomeratic sequence, which locally includes the lenses of limestone; and a sequence of mica and hornblende schists on top.

The quartzitic zone, wrote Emerson (1890, p. 373)

> "has passed through all the changes to a gneiss so complete that Professor Hitchcock insists on associating it with the Bethlehem gneiss."

The limestone is

> "for the most part coarsely crystalline, saccharoidal . . ., at times so coarse that cleavage pieces of calcite 8 centimeters across can be obtained from it. . . . It makes a strange impression to turn over a mass of coarsely crystalline limestone and find the weathered surface covered with crinoid stems or corals . . ." (p. 270).

From one point Emerson describes

> "distinct traces of corals and crinoids" in limestone that also contains some garnet, hornblende, and green mica", (p. 365).

The limestone is capped by a fine-grained magnetite layer, measured in inches rather than feet, that contains, besides magnetite and hematite and a little pyrite, such minerals as amphibole, biotite, and chlorite.

The overyling muscovite schist is rich in biotite and dodecahedral garnets and intercalated rather thick layers of "gray to black, fine-grained, wholly massive" hornblende rock, probably derived from limestone. At one place such hornblende rock contains "a bed nearly a meter thick of impure limestone", (p. 370) . . . carrying "abundantly light-colored garnet in large shapeless masses, and light green pyroxene" (p. 368).

In an introductory footnote, the aged J. D. Dana pointed the moral (Emerson, 1890, p. 265):

> "The paper will be accepted in America, and should be elsewhere, as putting the facts beyond doubt that gneiss, dioryte, granite, and the other crystalline rocks described are not always of Archaean or pre-Cambrian make; that dioryte and granites are not always of igneous origin; and these conclusions are made sure on the well-established criterion of age, that is, fossils—crinoids, corals, brachiopods."

He did not point out what to the writer seems the most significant aspect of this remarkable locality: many of the thick crinoid stems have retained their circular cross section. The specimens which the writer secured during a brief visit a few years ago show no recognizable form change. In thin section, the echinoderm texture is seen to be partly preserved.

New Hampshire

In 1870, C. H. Hitchcock discovered Silurian fossils in the vicinity of Littleton, N. H. (Hitchcock, 1871, p. 148). The Littleton-Moosilauke region has since yielded faunules from over a dozen localities. In a classical study, Billings has used them effectively to prove the stratigraphic identity of formations of different metamorphic facies in successive belts of increasing metamorphism (Billings, 1937, p. 486, 495, etc.). The beds of marble of the Silu-

[4] The only specimen specifically identifiable indicates Middle Devonian (Onondaga) age for the upper limestone (Balk, 1941, p. 2009).

rian Fitch formation, in which Hitchcock found *Halysites*, *Favosites*, and crinoid columns, are associated with calcareous quartz-chlorite-sericite 'slate" which carries a faunule of brachiopods, pelecypods, and trilobites (Billings and Cleaves, 1934, Pls. I, II). At the eastern-most locality (Billings and Cleaves, 1934, Fig. 1) crinoid columnals lie in marble that forms part of a series of "intricately crumpled" strata including mica schists and "a lime-silicate rock consisting of diopside, actinolite, andesine, and quartz" intruded by a basic dike altered to amphibolite (p. 418). Recently, Professor J. B. Thompson, Jr., and Arthur J. Boucot, one of Billings' students, found "unidentifiable zaphrentid corals" in the same general belt, about 3 miles east of Springfield, Vt., on Skitchewang Mountain in Claremont quadrangle, Vt. (Billings, oral communication).

More than 40 years after Hitchcock's discovery of Silurian remains, fossils were found in the overlying Lower Devonian Littleton formation (Lahee, 1912, p. 275). They lie in gray sandstone beds or lenses in dark slate which consists chiefly of quartz, sericite, chlorite, and albite (Billings, 1937, p. 488).

At the type locality where metamorphism has barely gone beyond the slate stage, most fossils are distorted and crushed by the deformation that produced the cleavage (Billings and Cleaves, 1934, p. 419, Pl. I, II). It is the more surprising, therefore, that two specimens of *Spirifer* were found in rocks of the highest facies of the Littleton formation seen in the region, rocks typical of the "katazone" of the Grubenmann-Niggli classification, injected by pegmatite dikes (Billings and Cleaves, 1935, p. 530–536). The dominant rock at the locality —Mt. Clough—is a mica schist, with sillimanite in many layers, partly replaced by aggregates of secondary staurolite.

One of the spirifers was found inside a metamorphosed, originally dolomitic, ellipsoidal concretion measuring 12 inches in the longest direction, parallel to the strike of the rocks. The composition of the center of the concretion differs from its outer shell and the surrounding schist. The three zones contain, in volume percentages: Central part: quartz 55%, clinozoisite 25%, diopside 12%, actinolite 5%, titanite 3%. Outer shell: hornblende 34%, garnet 12%, quartz 31%, clinozoisite 15%, bytownite 6%. Surrounding schist: quartz 60%, biotite 22%, andesine 10%, garnet (almandite) 8%. This specimen is shown in Figure 6 of Plate 1, reproduced from Figure 1 of Billings and Cleaves (1935).

The other *Spirifer*, here shown in Figure 5 of Plate 1 (Billings and Cleaves, 1935, Fig. 2), lies in a gneissic-looking rock made essentially of quartz (65%), andesine-labradorite (12%) and garnet (8%), with only 13% biotite. This mica content gives the rock a definite schistosity parallel to the bedding (Billings and Cleaves, 1935, p. 534). The position of the individual mica flakes oscillates about the plane of bedding, but maintains a common strike, producing a definite "lineation" on the bedding plane and a "girdle" about the direction of lineation in the petrofabric diagrams for biotite (Billings and Sharp, 1937, p. 290). This texture seems to be the rather inevitable result of a slight shortening at right angles to the axis of the girdle which would affect different mica flakes differently, depending on initial slight deviations from parallelism, assuming that the micas grew essentially parallel to the bedding.

The alternative, traditional view expressed by Billings and Sharp, that "slipping of individual sheets of minerals past one another seems to have been the most important mechanism of deformation", is practically refuted by the authors' admission that "the differential motion and consequent distention of the rock may be so slight that a fossil is not greatly distorted" (Billings and Sharp, 1937, p. 291).

How much distortion the shell has suffered cannot be told. Billings and Sharp estimate it as "at the most not over 25 per cent". That the total deformation is slight is shown by the petrofabric diagram for quartz in which the few scattered minute maxima amount to only slightly over 2 per cent.

Vermont

That "slipping of individual sheets of minerals past one another" is not an essential mechanism in the formation of schistosity in mica schists is shown by the specimen of a mold of a larger *Spirifer*, originally 8 cm. wide, found by Doll in a rather coarse-grained mica schist near South Strafford, Vermont. Figure 7 of Plate 1 (Doll, 1943, Pl. 1, fig. 1) does not

show the delicate detail of ornamentation seen in the specimen; viz., fine costellae on the broad ribs, shown best on the left side of the specimen, and wrinkly growth lines along the anterior margins of the shell (barely visible in the photograph).

The strong relief of the impression of the six major costae coupled with the preservation of delicate ornamentation in mica schist of such coarse grain leaves no room for significant differential slippage as a cause for the schistosity.

Yet the abnormal curvature of several costae shows that the specimen has been somewhat distorted. The deformation is like that of a mold in a block of wet clay that was squeezed out of shape, a distortion that affects the overall shape but produces no visible displacement of fine lines. But here again, the surprising fact is that the total form change is so small in a rock so highly metamorphosed.

The rock which contains the fossil consists of a quartz-muscovite-biotite schist with lesser amounts of orthoclase, oligolase, scattered zircon, and a few crystals of sillimanite associated with muscovite. Sillimanite and cyanite are present in gneisses and schists in the vicinity of the outcrop in which the fossil was found. The association of orthoclase, biotite, and cyanite and sillimanite places this rock at the threshold of the highest stage of metamorphism in argillaceous rocks (Barth, 1952, p. 333).

Doll (1943, p. 678) noted that the "specimen was embedded in a shallow, flat trough of a very gently plunging drag fold at its nose. The width of the brachiopod was parallel both to the schistosity in the rock and the axis of the fold." He suggests that in strongly deformed and metamorphosed rocks the "protected" portions of strata in the troughs and crests of drag folds should be likely places for the preservation of fossils. This is worth remembering.

In coarse-grained mica schist of the Shaw Mountain formation (Devonian?), Doll also found crinoid columnals. Thin sections made from specimens sent to the writer show the characteristic echinoderm texture well preserved in places, in the midst of coarse mica flakes. Recently Doll found not only stems, but "calyx molds" in crystalline limestone layers of the same formation, near Coventry, Vermont (Personal communication).

Recently Cady has found silicified cup corals in phyllites of the Waits River formation (Ordovician?) at seven localities 2 to 7 miles east-northeast of Montpelier, Vermont. The rock in which the fossils lie consists chiefly of sericite and very fine-grained quartz, small amounts of chlorite, and scattered megascopically visible ilmenite plates. Two of the localities lie a few feet west of a granitic sill. Near granitic sills, Cady writes (1950, p. 492),

> "increased metamorphic effects are quite apparent, particularly the appearance of spotted phyllite with porphyroblasts of biotite and cordierite. The limestone may be whitened and may contain considerable quantities of diopside and titanite."

The sericite flakes define a schistosity that strikes commonly at an angle that lies within 10° of that of the bedding (Cady, 1950, p. 494). The relation of cleavage to bedding and the orientation of the fossils suggest that the beds, which dip on the average 75° W., are overturned.

Further Examples of Fossils in Belts of Regional Metamorphism

General Statement

The occurrence of fossils in rocks of relatively high grade of regional metamorphism has been discussed in considerable detail, with two objects in mind: (1) to present two classical cases in sufficient detail to leave no doubt about the nature of the fossils and of the rocks in which they lie; and (2) to show that knowledge of the existence of such fossils goes back to the early days of geology, both in the Old and in the New World.

It remains to be shown that the examples given are not unique.

Central Appalachians

On the flanks of the Mine Ridge anticline, about 18 miles southeast of Lancaster, Pennsylvania, the lower Paleozoic formations have undergone rather intensive local metamorphism possibly related to the quartz monzonite and quartz diorite that appear as stock and dikes in the core of the plunging southern end of the anticlines (Knopf and Jonas, 1929, Pl. 1; Cloos

and Hietanen, 1941, Pl. 19). The degree of metamorphism decreases rapidly as one goes north from the Precambrian core of the anticline. This is well illustrated in the Harpers schist and overlying Antietam formation. Along the flanks of the Mine Ridge anticline, the lower part of the Harpers is a garnetiferous chlorite schist with biotite and subordinate quartz and feldspar. Its upper part and the Antietam schist are a gray coarse-grained, sparkling muscovite-biotite schist spotted with dull-white porphyroblasts of albite, with tourmaline, zircon, apatite, and calcite as common constituents (Knopf and Jonas, 1929, p. 47). In the upper part of the Antietam there is less albite and more calcite and dolomite, so that the rock is dominantly a calcareous biotite schist (Knopf and Jonas, 1929, p. 48). Toward the north and west these formations change within 5 miles to smooth phyllites below and more or less calcareous quartzites above, the common facies in Pennsylvania and adjacent States.

In the Antietam formation, half a mile north of the town of Gap and less than a mile from the Precambrian core of the anticline, fossils were found in rock carrying biotite (Knopf and Jonas, 1929, p. 50; A. I. Stose, oral communication).

On South Mountain, beds carrying *Obolella* and trilobite fragments weather to beds with characteristic rusty weathering. Similar rusty bands occur in the upper Antietam of the Mine Ridge anticline, here speckled with biotite (Knopf and Jonas, 1929, p. 46, 50). It is by observing such local and specific features that fossils can often be spotted when formations are traced from slightly to highly metamorphosed areas.

Trilobite remains were also found in metamorphosed Antietam on Madison Run, Orange County, Virginia (A. I. Stose, oral communication).

Southern Appalachians

Fossils have been found in the metamorphic Talladega series of Alabama and Georgia. In Alabama, remains resembling the algal genera *Cryptozoon* or *Graysonia* were found in white marble of the Sawyer limestone member, 3 miles west-southwest of Shelby, in Shelby County (Butts, 1926, p. 51, Pl. 9, fig. 17). This limestone lies about 4500 feet above the base of the Talladega series which consists dominantly of sericitic phyllites and reaches an estimated thickness of 30,000 feet (Butts, 1926, p. 50).

In northern Georgia, McCallie found imperfectly preserved fossils in marbles exposed some 3½ miles northeast of Elijah, in Gilmer County. Charles D. Walcott admitted their organic nature and suggested "sections of gastropod shells" (McCallie, 1907, p. 34). This "Murphy Marble", as LaForge and Phalen named it (1913, p. 7), overlies a zone of dominantly siliceous, micaceous, and talcose schists with andalusite, and even gneissose beds. A little to the north, in North Carolina, the same marble is overlain by calcareous muscovite-biotite schists rich in ottrelite (chloritoid) (Keith, 1907, p. 5).

Presumably higher in the series in Alabama a few specimens of poorly preserved marine fossils suggestive of Devonian age have been found in intercalated beds of chert and quartz schist (in Chilton County, Butts, 1926, p. 57–58) and quartzite (in Clay County, Griffin, 1951, p. 47).

The definition of the Talladega series included an upper sequence of practically unaltered dark shales which in Clay County, Alabama, has furnished remains of land plants, apparently of Pennsylvanian age (Smith, 1903, p. 244; Butts, 1926, p. 70). The absence of metamorphism in the "Erin shale" led to the interpretation that it must be exposed in a window among overthrust phyllites of the Talladega series (Jonas, 1932, p. 231; Park, 1935, p. 276; Crickmay, 1936, p. 1386). Griffin's detailed mapping shows this assumption to be unjustified (Griffin, 1951, p. 37–40). There seems to be an unconformity below the plant-bearing shales. Similar breaks in what seems at first sight to be a single "comprehensive" stratigraphic sequence are known from other orogenic zones. The upper part of the *Bündner Schiefer*, of Eocene age, for instance, is essentially indistinguishable from the Liassic lower part in the absence of fossils. In the Sierra Nevada, the Mariposa slates of Jurassic age are distinctly less altered mechanically than the otherwise very similar underlying Calaveras slates of Upper Paleozoic age.

British Columbia

A good example of the manner in which fossils appear unexpectedly in metamorphic terranes is contained in a report by Roots on the geology of an area in north-central British Columbia, between latitudes 56 and 57 and longitudes 125 and 126. He found Lower Cambrian Pleospongia (archaeocyathids) in "one small lense of limestone surrounded by chloritic phyllites" in the midst of a formation not less than 18,000 feet thick of quartz-chlorite and sericite schists and phyllites with interbedded crystalline limestones, quartzites, quartzitic conglomerates, and slates, which he calls the Ingenika Group, from its characteristic development in the mountains south and north of Ingenika River. The limestone lens was found 1140 feet below the top of an exposure of over 5000 feet of rocks of this formation. It pays to be alert even when the search for fossils seems hopeless (Roots, 1949, p. 178, 237, 279–280).

For comparable occurrences of Pleospongia in British Columbia the reader is referred to Okulitch's memoir (Okulitch, 1943).

Cuba

In the Antillean region, the fossils in the Cayetano formation[5] of western Cuba, in the province of Pinar del Rio, come readily to mind. Beautifully preserved ammonites of early Upper Jurassic age are found at several localities in lenticular limestone or siltstone concretions in the midst of unfossiliferous phyllites with interbedded quartzitic sandstones and marbles which reach a great thickness (Dickerson and Butts, 1935, p. 117; Imlay, 1942, p. 1421–1423). On the whole, the degree of metamorphism seems to be quite low and local (Palmer, 1945, p. 10), probably near the lower limit permissible for inclusion in this review.

Venezuela

Metamorphic rocks make up a large part of the northern ranges of Venezuela between Barquisimeto and the Gulf of Barcelona and their continuation in the coast range of eastern Venezuela. As early as 1861, Karsten suspected that most of these metamorphics, which range from phyllites to gneisses, are altered equivalents of the thick sequence of Cretaceous formations that surround them on the west and south sides. Though growing knowledge of the stratigraphy of the Cretaceous sediments and of the metamorphics beyond them made it increasingly probable that this interpretation is correct (Kehrer, 1938, p. 59–66), it had by no means been generally accepted in 1945 when the writer studied the structure and orogenic history of Venezuela (Bucher, 1952, p. 39–51). Fossils were needed to clinch this point. In 1943, Wolcott found megafossils in gray limestone in the eastern part of the western Caribbean Mountains (Coast Range) (Wolcott, 1943, p. 1632). The writer saw the material in 1945. Since the matrix looked unmetamorphosed and metamorphism seems to decrease eastward toward the coast in general, he was left in doubt concerning the relation of this horizon to the metamorphic series. In the meanwhile, Hess and Dengo have revisited the locality. In a letter (1952) which brought the writer all the information on recent Venezuelan fossil finds mentioned below, Hess gives the following valuable details: the fossils are in place at a waterfall over a hard quartzitic zone in schist (probably the Cretaceous Las Brisas formation).

"The quartzite is severely sheared and recrystallized. In it lie small lenses of black limestone (1 by 3 feet). These are commonly brecciated internally, while outwardly maintaining the lense form. The fossils are preserved in less deformed 'shadow' zones in the matrix of the breccia."

(*See also* Dengo, 1951, p. 72–73.)

Later Dusenbury and Wolcott found poorly preserved forams and radiolarians in fine-grained recrystallized impure gray limestone (Dusenbury and Wolcott, 1949, p. 17–26; Dengo, 1951, p. 72–73). According to Dusenbury the forams indicate a Turonian age. He correlates the series with the Los Colorados member of the Las Mercedes formation.

Hess found fossils in a pebble from a conglomerate within low-grade phyllites ("Paracotos formation") on the road from Charallave to Caracas. The forams have been identified as

[5] DeGolyer, who named the formation, introduced the form "Cayetano formation" (1918, p. 140) and not the enlarged form, "San Cayetano formation," lately used.

Turonian by Renz. Forams of the same age (reported in Smith, 1953) were found by MacLachlan, one of Hess' students, on the La Rosa road east of Villa de Cura, in limestone beds lying in phyllites (MacLachlan, 1952).

Hess found forams of either Paleocene or late Cretaceous age in the Villa de Cura limestone, at Villa de Cura. The limestone itself is thoroughly recrystallized. The fossils are preserved in the matrix of brecciated zones (letter to the writer, 1952).

The lithology of the limestone layers, in which most of the fossils are preserved, is worth noting. They are fine-grained and bluish gray, suggesting that they may have contained organic matter. The writer does not know what this suggestion is worth. But such limestones do turn up rather frequently in metamorphic terranes; they have somehow escaped recrystallization such as has changed other beds to coarser white marbles, and it is in them that fossils are apt to have been preserved. A comparative study of the limestones in a metamorphic sequence, where some are recrystallized and some still fine-grained, with their counterparts in an adjoining unmetamorphosed belt will eventually bring to light the reasons for this different behavior.

Scandinavia

The discovery of Silurian fossils in metamorphic rocks south and east of Bergen in Norway by Reusch in 1881 (1883, p. 62) did for Scandinavia what the discoveries presented in the first part of this paper did for the Alps and for New England. It did away with the tendency to connect metamorphism with great age.

Corals (*Halysites*, *Favosites*, etc.), graptolites (*Rastrites*, *Monograptus*), unidentifiable brachiopods, and remains of trilobites (*Calymene*, *Dalmanites*) were found as rust-colored molds in a light-colored, glossy muscovite-biotite schist east of Bergen. For the regional setting of the Silurian belts, see the very useful map of "The Scandinavian Caledonian Zone," by O. Holtedahl, in Bailey and Holtedahl (1938, Pl. II (1:2,500,000)). Some 8 km. south-southeast of the city, the same corals and also *Cyathophyllum* and unidentified gastropods lie in nodular gray marble beds intercalated in dark phylite. These beds alternate with layers of granulitic gneiss (locally with garnet and hornblende), conglomerates with stretched pebbles, talcose marble, and hornblende schist. In the railroad cut east of Trengereid (the southern locality) 22 such units, standing nearly vertical, succeed each other in a distance of about 200 meters (Reusch, 1883, p. 69–70, esp. Fig. 52, p. 69).

The trilobites (Reusch, 1883, Figs. 46–47, p. 66) and brachiopods in the mica schist are distorted, like those in the Littleton formation of New Hampshire. Other fossils, especially some of the corals (*e.g.* *Cyathophyllum*, Reusch, 1883, Fig. 49) and graptolites, are almost undeformed.

Rather well-preserved fossils were found over 900 kms. to the northeast, 12 kms. south of the second highest peak of Norway (Mt. Sulitelma, elevation 1914 m.) practically on the Swedish-Norwegian boundary (approx. 16½° E. Long. and 67° Lat.). The first fossils, crinoid stems, were found by G. C. v. Schmalensee and described by Sjögren (1900, esp. Pl. 4). Additional remains, especially well-preserved bryozoan colonies of the genus *Dianulithes*, were found by Vogt (1927, Pls. 20, 21).

Vogt has given a detailed map and section of the vicinity of the fossil localities in his classical work on the Sulitelma region (Vogt, 1927, p. 51–67, with English summary, p. 456–457, and map, Pl. 38). His map of the metamorphic zones (Pl. 39) shows that the fossil localities lie in a narrow zone of lowest degree of metamorphism, surrounded by more strongly metamorphosed rocks. Vogt found the crinoids and bryozoans in 10 horizons in limestone layers not more than a few meters thick that are associated with black schists overlain by green chlorite and brown biotite schists, all dipping about 30° beneath the Sulitelma gabbro "phacolith" (p. 457 and Fig. 13). Vogt believes the sections were repeated several times, in folds strongly overturned toward the south (Fig. 15), away from the gabbro intrusion. Less than 1 km. north and south of the fossil localities, garnet (almandite) appears in the schists.

Italy

About half way between Genoa and Florence, the Apuane Alps rise abruptly to a height of 2000 m. behind a narrow coastal plain, exposing

late Paleozoic, Mesozoic, and Tertiary strata in great asymmetric folds (Lotti and Zaccagna, 1881, two plates oppos. p. 32; Zaccagna, 1891–1896; 1893–1896). In these anticlines, Paleozoic and Triassic formations have been changed to crystalline rocks, the degree of metamorphism increasing with the sharpness and crowding of the folds (Lotti, 1888, p. 407). The pre-Liassic crystalline rocks consist of the following sequence (Lotti and Zaccagna, 1881, p. 9):

(*top*)

(4) Schists alternating with micaceous limestones and lenses of crystalline limestones (1000 m.).
(3) Saccharoid marble and crystalline dolomite (thickness variable, but may reach 1000 m.). This contains the world-famous marbles of Carrara.
(2) Fissile limestones and gray compact and "brecciform" limestones (200–600 m.).
(1) Mica schists, talc schists, and gneissose schists with lenses of calcareous schists.

(*bottom*)

In (1) small lenses of gray calcareous schists have yielded *Orthoceras* and *Actinoceras*, which places them in the Paleozoic. From (2) gastropods of undoubted Triassic age have come. The great marbles of (3) showed only unidentifiable crinoid remains and sections of gastropods. The upper schist (4), on the other hand, is rich in crinoids, especially *Pentacrinus*, and contains ammonites sufficiently well preserved to be at least generically identifiable (*Phylloceras*, *Aegoceras*).

Russia

The crinoids which Murchison, De Verneuil, and Von Keyserling found in crystalline limestones in the midst of a typical metamorphic sequence, in the southern Urals, are among the stock examples quoted in the earlier geological literature. They were found in the valley of the Upper Miyas River, east of Zlataust, in the region crossed today by the South-Ural Railway. The passage describing this discovery deserves being quoted:

"... after following the ... valley of the river Miass, with the gneissic ridge of the Ilmen-tau on the east and the higher eruptive and metamorphic chain of the Ural-tau on the west ... we discovered *Encrinites* in pure white saccharoidal limestone. So highly altered is the rock, that we could still less believe our eyes, than when many years ago in the Austrian Alps, with Professor Sedgwick, we discovered similar organic remains in the chloritic, primarized limestone in the Tauern Alp. (Geol. Trans., Vol. III, p. 306). This limestone ... left no option but that of admitting that the associated stratified masses, however crystalline they may now appear, were once quartzose sandstones and greywacke ..."

(Murchison, *et al.*, 1845, p. 426). A few pages later, "mica schists," "serpentine with hornblende slates and chloritic quartzose schists" are mentioned as typical of the crystalline rocks associated with the marbles (p. 434–435).

On his geological map of the region, Tchernyshev marks this belt as crystalline schists with bodies of serpentine and granite. In the text he characterizes the sequence as follows (Tchernyshev, 1889, p. 336; translated from the German abstract):

"In the crystalline complex M quartzites lie on top and below them a series of phyllites, mica schists, chlorite schists, etc., in which marble-like limestone layers ... characterized paleontologically, lie intercalated."

He emphasized that the transition of the unmetamorphosed Devonian sediments into the crystalline schist series M is so gradual and inconspicuous that the boundary between the two colors on the map is arbitrary (p. 337), and that A. Karpinski had come to the same conclusion in the same belt farther north.

The crinoidal limestones are not mentioned in the brief reference to the crystalline schists of the region in the Guidebook of the Uralian Excursion, issued during the 17th International Geological Congress (Koptev-Dvornikov 1937, p. 113–122), and the schists are referred to as Precambrian. A paper by Kuznetzov (1939, p. 151–160) explains the change:

"Tchernyshev's opinion supported by erroneous correlations was firmly rooted in the Russian literature and accepted since that time as a fact. ... Fundamental changes in opinions concerning the age of the crystalline schists in the Central Range occurred during the last ten years, after the necessity of creating in the Soviet Union a heavy industry ... has caused a wonderful progress of geological and quest work. ..."

Perhaps the history of science should be expected to progress in the Urals in the opposite direction to that of the West. Why, then, bother about crinoids?

Japan

The Sambagawa system forms a narrow belt along the outer side of the so-called Median Dislocation line of Japan. It consists chiefly of crystalline schists and intercalated metamorphosed basic igneous rocks. The view of the pioneers of Japanese geology, who called it "Archean," prevailed until 1937 when Kobayashi suggested that they may be metamorphosed equivalents of the Paleozoic Chichibu group (Kobayashi, 1944, p. 159). Shortly thereafter, Huzimoto discovered radiolarians in crystalline schists in it near Nagatoro in the northeastern mountains of Kwanto (Huzimoto, 1938, p. 252).

The Sambagawa system comprises three divisions: a lower one of sericite schist and intercalated piedmontite schists; spotted graphite-sericite schist and chlorite amphibolite in the middle; and epidote-sericite gneiss on top. The microscopic skeletons (0.1 to 0.2 mm. long) lie chiefly in minute calcareous lenticles, less than 3 mm. long and 1 mm. thick, which lie scattered along planes of schistosity in layers of sericite schist intercalated in a sequence of interbedded greenschists and hematite-quartz schists of the Middle Division (Huzimoto, 1938, p. 252–253). Huzimoto thought the radiolarian fauna of the Sambagawa system resembled closely those described from Europe, Borneo, and Japan, formerly thought to be Jurassic, now assigned to the "Permo-Triassic or thereabout" (Kobayashi, 1944, p. 161). Suzuki found essentially the same fauna in rocks of the Hidaka and Kamuikotan systems of Hokkaido from which poorly preserved fossils of seemingly upper Paleozoic age had been collected (Suzuki, 1939, p. 56–59). In the same year, however, Yabe and Sugiyama (1939, p. 86–89) described a typical Mesozoic hexacoral from a "green schistose rock" which they thought came from the Kamuikotan system, a correlation which, in turn, was made to appear doubtful by Harada (Kobayashi, 1944, p. 160). Kobayashi has discussed the question of the age of these radiolarian faunas in his learned paper *Radiolarian rocks* (1944, p. 159–163). The question is of interest chiefly because it illustrates how difficult it is to make the transition in thought from "Archean" to "Mesozoic", when fossils are found in metamorphic rocks.

In Kobayashi's argument about the possible age of the radiolarian faunas, theoretical doubts concerning paleogeographic and facies play an important role. The difficulty of seeing relatively coarse clastics and radiolarian-bearing rocks in one and the same sequence was here discussed on an earlier page in connection with the Devonian of Alsace. The relations between paleogeography and the orogenic cycle are still far too vague to permit considerations based on them to be used in correlation.

In some Japanese cherts, as in those of other regions, radiolarians are changed to chlorite. The chloritization seems to proceed faster in some forms than in others (Kobayashi and Kimura, p. 132).

Recently a crinoid limestone has been reported from crystalline schist (Huzimoto and Yamada, 1949). Unfortunately, the paper is not available to the writer, whose attention was called to it by Professor Kobayashi.

The examples presented so far lie in belts of regional metamorphism with no, or at least no obvious, relation to plutonic rock bodies. We turn now to fossils found associated with minerals typical of the contact aureole of granitoid intrusions.

Fossils in Contact-Metamorphic Rocks

Brittany and Normandy

In view of what is recorded on the preceding pages, it is not surprising to find typical contact minerals side by side with fossils in the contact zones around granites. Northwestern France has furnished the most famous examples where chiastolite crystals lie conspicuously interspersed with fossils in altered Ordovician shales. The classical locality is Salles-de-Rohan, east of Carhaix, in the heart of western Brittany. Here the sharply defined dark-centered, lozenge-shaped cross sections of the chiastolite crystals, which stand out conspicuously as spots (maculae) on rock surfaces, were objects of curiosity during the Middle Ages. They

are mentioned in print as early as the fifteenth century.[6] In 1838, Puillion Boblaye discovered fossils associated with chiastolite crystals in the same rock (Boblaye, 1838, p. 186). Others soon confirmed his observations and described geology and rocks in detail. (*See especially* Durocher, 1846, p. 552; Barrois, 1886, p. 854–857.)

According to Cross (1881, p. 382–384; Barrois, 1886, p. 857), these chiastolite-bearing schists of the Salles-de-Rohan consist of a fine-grained groundmass of quartz and sericite made dark (almost black in the hand specimens) by quantities of "carbonaceous" matter, with chlorite, ilmenite, scattered tourmaline and rare rutile, and, of course, the large crystals of chiastolite. A specimen that Lacroix figures in his text (1893, Fig. 23), here reproduced as Figure 1 of Plate 2, shows the strange juxtaposition of fossil and mineral. Note that the chiastolite crystal near the base of the specimen is 7½ inches long. It may be significant that trilobites are chiefly mentioned among the fossils (*Calymene, Trinucleus, Dalmanites*).

Count de Limur (1885, p. 55) mentions that, farthest from the granite, the fossils are best preserved, and the chiastolite crystals poorest; toward the contact, the fossil impressions become less distinct, while the crystals reach their finest development.

Barrois points out that this locality lies more than 3 km. from the contact with the granite and thus illustrates strikingly "the irregular and capricious manner in which the metamorphosing effect of the granite is propagated" (Barrois, 1886, p. 857; translated. *See also* his structure section, p. 855.).

[6] According to Barrois (1886, p. 856). In his compendious *Mineralogy of France* Lacroix figures the seal of a Vicomte de Rohan, dated 1222, which shows the "maculae" in his coat of arms. He quotes authoritative opinions that the "mascle" of heraldry may have had its origin here.

In a well-known paper on the granite of Flamanville, on the west coast of the Cotentin peninsula of Normandy, Michel-Lévy (1893, p. 1–41) gives a graphic picture of a similar contact zone. Here, the Early Paleozoic argillaceous rocks are feldspathized near the contact with the granite, while some distance away they contain crystals of chiastolite, pointed octahedrons of secondary anatase, rutile needles and biotite in a mass of fine quartz grains, together with impressions of trilobites (*Calymene*) (Michel-Lévy, 1893, p. 4, 11).

Nevada

In the Yerington mining district, about 40 miles east of Lake Tahoe in Nevada, the oldest exposed rocks are Triassic sediments and volcanics. The sediments consist principally of limestone and quartzite. About the end of Jurassic time, this rock sequence was folded and intruded by large masses of granodiorite and quartz monzonite. For a considerable distance from the contact with these intrusive rock bodies, the sediments were changed to complex series of lime-silicate rocks. Their nature is well shown by the detailed section recorded from the northwest slope of Douglas Hill, in Adolph Knopf's masterly report on the region (Knopf, 1918, p. 17, Fig. 2). From the base to the top, the sequence is as follows (thickness given in feet):

(top)	i. Garnetite	(about 300 feet to top of hill)
	h. Fault breccia, cemented by andradite	(about 20)
	g. Felsites, lime silicate rocks, and garnetites	(about 70)
	f. Black epidote-vesuvianite rocks	(about 280)
	e. Aphanitic tremolite rock	(about 75)
	d. Black lime-silicate rocks	(about 150)
	c. White lime-silicate rocks	(about 450)
	b. Limestone	(about 250)
(Bottom)	a. Quartzite, highly brecciated	

"Although these rocks are highly metamorphic they are well stratified and retain their general aspect of sedimentary rocks. The fine-grained rock near the base of the belt of white lime-silicate rocks (c) consists chiefly of wollastonite, with accessory plagioclase (Ab_{75} An_{25}), diopside, and pyrite. The finely banded aphanitic hornfels (e) . . . proves to consist largely of slender fibres of tremolite scattered through a feebly birefringent granular aggregate, which probably consists of plagioclase. . . . The uppermost belt of black hornfelses (f) . . . consist of heavy aphanitic rock . . . . made up largely of vesuvianite . . . and epidote of a pale variety near clinozoisite. The black color of the rock is due to

very abundant and finely disseminated carbonaceous matter." Higher up, an aphanitic hornfels consists "of vesuvianite, diopside, and quartz. Near the top of the section there occur garnetites which are composed solidly of microcrystalline garnet . . . nearly pure grossularite."

"The fact that the appearance of normally stratified rocks is preserved by the dense aphanitic wollastonite rocks and garnetites suggests that large amounts of silica, ferric oxide, and possible other substances were added during metamorphism and that the volumes of the original strata have remained unchanged. This conclusion appears to be confirmed by the discovery of a completely garnetized fossil in the stratified garnetites near the McConnell mine . . . identified as *Halobia*" (Knopf 1918, p. 17).

This garnet is a variety about halfway between grossularite and andradite (p. 16). The *Halobia* specimen is here reproduced as Figure 2 of Plate 2 (from Knopf, 1918, Pl. 2, Fig. A). Knopf[7] concludes that the garnetization of the *Halobia* and its matrix took place "without change in volume or increase of porosity" and "must therefore have involved the addition of large amounts of ferric iron, silica, and probably alumina to the metamorphosed limestone from an extraneous source". How far this is true could possibly be determined by a careful microscopic and chemical study of the equivalent unmetamorphosed sediments. The sequence is rich in volcanic rocks, which makes it possible, if not probable, that the limestones contained admixed volcanic matter. A comparable situation is involved in the example that follows.

Alsace

Instructive cases of replacement by silicates have been reported from the contact aureoles of granites in the Paleozoics of the Vosges Mountains of Alsace, one of the classical regions for studies in contact phenomena. Jean Jung has given a comprehensive summary of the region's varied geology, with a geologic map in colors (1:200,000), to which the reader is referred for localities and areal relations. The observations were all made along the northwest border of the northernmost of the Vosges granites, the granite of Champ du Feu.

The first locality lies close to the granite contact near the village of Rothau, in the Valley of the Bruche River. This valley lies in a series of Middle Devonian sediments which is dominantly clastic and shot through with andesitic lavas and tuffs, particularly in the country around Rothau. Somber-colored graywackes, consisting of detrital sand grains mixed with volcanic fragments and tuffs, are the most abundant and characteristic elements of this part of the Devonian sequence. Limestones, consisting chiefly of fore-reef fossil breccias and lenses and beds of related origin, lie intercalated within them. Fossil fragments, masses of reef breccia, have locally become mixed in with the tuffs and tuffaceous graywacke material (Jung, 1928, p. 243-244).

In 1844, A. Daubrée found near Rothau calcareous rocks of this series completely transformed into a mass chiefly of "lamellar pyroxene, epidote and dense garnet, with specs of galena," for a distance of several hundred meters from the granite contact. In the midst of this rock, made up completely of these silicates, he found perfectly preserved impressions of *Favosites* ("*Calamopora*") and other corals. The cavities left by the disappearance of the calcitic material of the skeletons are lined with crystals among which quartz and needlelike crystals of a black amphibole are conspicuous, together with a green garnet and axinite (Daubrée, 1844, p. 408–410; 1857, p. 318; 1879, p. 138–144). Remnants of the original calcitic material lie in the midst of these silicates here and there.

The writer has seen no references to more recent studies of this remarkable contact zone, with one exception. Elisabeth Jérémine (1933) has described startling cases of the replacement of fossils by silicates from the southern contact of the same granite, some 10 miles southwest from Rothau, southeast of the little town of La Grande Fosse.

Here a very fine-grained limestone of the same general stratigraphic level as the Devonian sequence has been transformed into a scarn consisting of pyroxene with garnet or amphibole. In a matrix of minute grains of

[7] Knopf quotes other illustrations which will be merely mentioned here. There must be many more in the literature. Lindgren (1913, p. 671) reports that "at Tres Hermanas, New Mexico, near the contact with granite porphyry, spirifers and fenestellas have been perfectly preserved in the garnetized rock." Goldschmidt (1911, p. 327) found that in some of the contact-altered limestones in the Oslo region thick-walled brachiopod shells have been completely altered to wollastonite.

quartz, feldspar, and calcite, full of minute fibers of amphibole, regularly shaped bodies that are round, oval, or elongated stand out when seen in normal light. They are more transparent and cleaner looking than the matrix. They look like chance sections of fossils. That they really once were organic remains is shown conclusively by the reticulate texture of many grains which is so typical of echinoderm skeletons. But they consist now of diopside and epidote, in rather coarse crystals! The altered fossil remains are characteristically surrounded by an aureole of closely packed grains of pyroxene, amphibole, and epidote. (Jérémine, 1933, p. 97). Jérémine's photographs that accompany her description are here reproduced as Figures 3 and 4 of plate 2 (Jérémine, 1933, Pl. II).

One other type of contact-metamorphic alteration from the northern border of the same Champ-du-Feu granite deserves attention. The rocks affected are fine-grained beds of radiolarite which appear interbedded with tuffs and tuffaceous graywackes in the Devonian of the Bruche valley. Jacques de Lapparent has described this strange association in a number of papers (1919; 1920; 1923a; 1923b). These are summarized in his extraordinarily valuable *Leçons de pétrographie* (De Lapparent, 1923b, p. 315–318). Many of the fine-grained radiolarites form the top of a graded sequence of tuffaceous layers that are quite coarse at the base. Thin sections show that they consist chiefly of very fine-grained tuffaceous material in which the radiolarians lie in streaks. Skeletons of radiolarians are also found mixed in with rather coarse tuffaceous materials. De Lapparent reproduces a beautiful slide of such a specimen in the midst of crystals in a tuff (Pl. 11, fig. 7, opp. p. 260). He finds that the substance of the skeleton has been changed from the original opal to an "iron alumosilicate which has the properties of a chlorite" (p. 259). He affirms that he found this to be true in all Paleozoic radiolarites. The interior of the minute spherical skeletons is normally filled with chalcedony. But in the Bruche valley, near the granite, a mixture of albite and quartz takes the place of the chalcedony. De Lapparent believes that this substitution took place in the course of diagenesis, which would not seem strange in a tuffaceous environment (De Lapparent, 1923b, p. 318).

The transformation produced in radiolarites near the granite contact was observed by Jérémine about 14 miles southwest of Rothau, in the valley of the Rabodeaux River above the town of Moyenmoutier. Here a green, highly pleochroic biotite fills the interior of the skeletons, in many cases intergrown with muscovite, chlorite, and albite. The skeleton itself forms a transparent ring perforated by the pores that are filled with green chlorite and biotite. An envelope rich in micaceous material forms a metamorphic halo around each skeleton. This is well shown in one of Jérémine's figures (1933, Pl. 1, fig 3), here reproduced as Figure 5 of Plate 1. In some way, each little skeleton has acted as a catalysing agent of metamorphism, initiating the formation of micas in its immediate surroundings, ahead of the transformation of the whole rock. Jérémine gives reason to believe that, as metamorphism progresses, the outline of the skeleton will vanish but leave minute circular clusters of coarser mica in a finer micaceous matrix as shadows of their former existence (Jérémine, 1933, p. 96).

Significance

Why Fossils are Preserved in Regional Metamorphism

Ever since Sorby, Tyndall, and Daubrée, almost a century ago, produced in clay a texture that megascopically resembles slaty cleavage, by rolling the clay out or forcing it through orifices[8], geologists assume rather generally that mechanically impressed movement, accompanied by rotation of grains and slippage within the mass, plays an important part in the production not only of cleavage, but of schistosity as well. In his recent memoir on metamorphic rocks, Turner (1948, p. 275), for instance, defines schistosity as follows:

> "When a parallel fabric of this kind, originating through *penetrative movement* that has intimately affected the component fabric elements, imparts to the hand specimen a recognizable fissility, the rock is said to be schistose."

[8] For references to this early literature, *see* Daubrée, (1879, p. 407-426) and Jannettaz (1884, p. 211-236).

To be sure, Turner uses the word "movement" in Sander's sense, distinguishing between "direct componental movements involving crystal gliding or relative displacement of grains, and indirect movements, which include transport of atoms and ions. . . ."

But, whether intentionally or not, in connection with metamorphism the very choice of words suggests something different from what happens when a pyrite crystal changes to limonite or a limestone is replaced by chert or dolomite, or, for that matter, when anorthite or diopside crystals grow in parallel orientation in a cooling cube of glass, subject to differential pressure, producing a schistose texture by crystallization only, without much visible deformation of the cube[9].

Yet nothing more, and certainly no differential movement or flattening out, entered into the production of the schistosity within which lie some of the fossils described above. The high relief of the costae on the *Arietites* (Pl. 1, fig. 1) and the *Spirifer* (Pl. 1, fig. 7) and the sculptural detail on the latter leave no doubt about that. In the former, the mica flakes that produce the schistosity are relatively coarse; in the latter, they are minute. In neither can there have been any mechanical "Durcharbeitung." The transformation from the original rock cannot have been different in principle from the process involved in the dolomitization of a limestone. This comparison is more to the point than may appear at first, as an example will show.

The Silurian Bisher dolomite of Southern Ohio was derived from a medium-grained, fossiliferous calcarenite. The texture of the original material is preserved in occasional flat lenses of a white chert, typically a number of inches across and a fraction of an inch thick, which replaced it at a very early stage of diagenesis. In thin sections, and especially on weathered surfaces, every detail of the texture of the original calcarenite may be seen: quantities of rounded shell fragments, beautifully preserved ostracods, head and tail shields of trilobites, and small brachiopods[10]. On large pieces of chert one sees occasionally a large brachiopod.

The fine- to medium-grained crystalline dolomite that took the place of the calcarenite as diagenesis progressed shows no trace of this original texture nor of the delicate fossil remains in which it abounded. It consists of a tightly packed mass of equidimensional idiomorphic crystals of dolomite. Only here and there, at a few horizons in the Bisher dolomite, rather large, convex brachiopod shells (*Schuchertella, Stropheodonta, Whitfieldella*) and head and tail shields of big trilobites (*Dalmanites*) are preserved as molds, the details of their ornamentation impressed on the crystalline matrix. That molds of such large shells have survived the complete recrystallization of the original calcarenite is no less remarkable than the survival of brachiopod and ammonite molds in schists, though only a single chemical reaction was involved. Fundamentally, the processes must have been the same in the carbonate and silicate rocks.

That silicates, even those labeled "stress minerals", enter into replacement reactions under unstable conditions is shown by the contact metamorphism at Rothau and Yerington. If such things seem incredible to us we must remember that processes are not impossible just because the difficult laboratory techniques needed to test them have not been achieved yet. Actually, ingenious research now going on in the United States and England has obtained highly pertinent results already.

The conclusion seems justified that typical metamorphic rocks, such as chlorite and mica schists, can form as a result of recrystallization alone, with or without introduction of atoms and ions, in the presence of pressure differences that give direction to crystal growth, but need not produce differential movements. This does not mean that in many, perhaps most, cases mechanical effects did not play a role also, at least on the microscopic scale. But they are incidental, not essential to the production of schistosity in metamorphism. That is why

[9] F. E. Wright's elegant experiment, which was designed to prove qualitatively that differential stress has a directing influence on crystal growth, deserves attention (Wright, 1906, especially Figs. 1–3, p. 227–229).

[10] Foerste, A. F. (1917) *Notes on Silurian fossils from Ohio and other Central States*, Ohio Jour. Sci., vol. 17, p. 187–204, 233–267. The chert lenses and their ostracods are briefly described in E. O. Ulrich and R. S. Bassler (1923) *Paleozoic ostracods: their morphology, classification and occurrence, in Silurian volume*, Maryland Geol. Sci., p. 389–391.

fossils are not destroyed by metamorphism, provided they are much larger than the average size of the newly formed minerals.

To most students of metamorphism this is, of course, not a new thought. But it needs renewed emphasis, since it leads to conclusions that go further than is generally realized.

Why Fossils are Rare in Regionally Metamorphosed Rocks

If large fossils had been as abundant in the sediments that became the metamorphic cores of orogenic belts as they are in many a formation of the continental platforms, their molds should be fairly common in metamorphic terranes. But they are not.

To some extent this rarity may be more apparent than real, for good psychological reasons. First, metamorphic rocks are hard. If the typical sedimentary rocks were as difficult to break as fresh garnetiferous mica schists or sillimanite gneisses are, our knowledge of fossil faunas would be mighty meager. Moreover, in metamorphic rocks fossils are poorly preserved. Now paleontologists do not care for poorly preserved fossils, and narrowly trained "hard-rock geologists" do not care for fossils. Since those who know where to find fossils are unwilling to look, and most of those who are looking at the metamorphic rocks do not know what to look for and where, much valuable material must remain undiscovered.

But even so, the total number of fossils recorded after 150 years of search is too disproportionately small to allow any other conclusion, but that the larger types of fossils were rare in the original sediments.

Observations in the unmetamorphosed or only slightly altered equivalents of the crystalline rocks in orogenic belts bear out this conclusion. Shells of benthonic animals, especially the larger brachiopods or mollusks, are very rare indeed in the Ordovician shales of the northern Appalachian geosyncline ("Hudson River shales"). Even the rather rich graptolite faunas are limited to thin bands of dark shale that constitute only a small fraction of the total thickness.

In the Sierra Nevada, the age of the thick sequence of dark shales in which the fabulous gold veins of the Mother Lode system lie was long unknown until, in 1864, Clarence King discovered the belemnites in it, and thereby solved the mystery[11] (Whitney, 1865, p. 482).

The metamorphic alteration of the shales in the Sierra Nevada geosyncline is distinctly greater in the late Paleozoic Calaveras shales which are said to be separated from the overlying Mesozoic shales by an unconformity. Here, the dark argillaceous rocks are glossy slates or phyllites, with grains of quartz in quartzitic layers flattened, etc. (Knopf, 1929, p. 11). But here, also, fossils are rare and limited largely to gray limestone lenses intercalated between layers of shale.

The same is true of the *Bündner Schiefer* outside the metamorphosed zone described earlier in the paper. The comparison with the Calaveras-Mariposa shales of the Sierra Nevada and comparable geosynclinal series elsewhere is very striking. It extends to the association with greenstones, the presence of beds of fine-grained sandstones, cherts, lenses of gray, fine-grained limestone, to which the rare fossils are largely limited, and even to the long time-break between the upper and lower series referred to above.

It is not necessary to multiply examples. But it pays to emphasize the conclusion that must be drawn from the habitual scarcity of benthonic fossils, and of fossils in general, in geosynclinal sediments. A careful analysis, for which this is not the place, leaves little doubt that, of all possible factors, considerable depth of water is the one that will reduce the benthonic

[11] When, half a century later, Clarence King told the story of this historic discovery in his spirited *Mountaineering in the Sierra Nevada*, he marveled that these belemnites should have survived the "... ordeal of metamorphism" (King, 1911, p. 220–223). These words might have been placed as a motto at the beginning of this paper as an expression of the widespread prejudice that has prompted this paper. Yet the mechanical and chemical effects to which the Mariposa shales were subjected, which contain the belemnites and other fossils found subsequently, are so slight that they do not warrant inclusion in this discussion. Within half a mile and more of the contact with intrusive cores of granite or granodiorite, the shale is, of course, changed to sericite schist as, *e.g.*, in the area of the Big Trees folio of California (Turner, 1896, p. 536) and the Pyramid Peak folio of California, where rocks assigned to the "Juratrias", west of Tello Peak, are "strongly metamorphosed and ... composed of gneissoid schists, quartzites, and mica-chlorite-andalusite schists" (Lindgren, 1896, p. 4). In such zones fossils should be sought.

fauna drastically, no matter what sediment accumulates on the sea floor. In many dozens of deep-sea cores from the Atlantic and the Caribbean Sea that Maurice Ewing has secured and split open for study, no remains of organisms have been found larger than forams and planktonic pteropods, with one exception. In the distant portion of the submarine canyon of the Hudson River, 180 miles from the shore, and 60 miles[12] beyond the foot of the continental slope, at a depth of 11,382 feet, (3470 m.), numerous fragments of typical shallow-water marine pelecypods and gastropods of still existing species (Pleistocene?), together with pebbles up to half an inch in length, were found intimately mixed with globigerina-rich deep-sea clay. The circumstances point compellingly to a turbidity current, produced by a submarine landslide as the depositing agent (Ericson Ewing, and Heezen, 1952, p. 489; Heezen and Ewing, in press). Kuenen's brilliant application of Daly's concept of turbidity currents to the problems of sedimentation (Kuenen, 1951, p. 14–107; 1952, p. 28–36) is shedding a flood of light on many of the most perplexing problems of geosynclinal[13] sediments; such as, for instance, the association of radiolarites with coarse detrital sediments in the Devonian of the Vosges, mentioned earlier.

As geological information and understanding grow, the concept of an initial geosynclinal stage in the development of an orogenic belt (Bucher, 1933, p. 125–139) appears increasingly justified, a stage in which the geosynclinal floor sinks faster than sediments accumulate. This produces a marine trench of sufficient depth to prevent occupation by a normal marine benthonic fauna and invites the operation of those processes which result in the peculiarities of sedimentation and stratification so generally found in the corresponding portions of geosynclinal sediments.

[12] The figures given are nautical miles. They are, respectively, 207 and 69 statute miles.

[13] Throughout this paper, the writer uses the word "geosyncline" for relatively long and narrow depressions of the earth's crust, the floors of which ultimately sink to depths greatly in excess of the normal depth of the larger basins in which they lie. ("Orthogeosynclines" of Stille and Kay).

Speculations

This brings us back to the crucial fact that regional metamorphism begins and centers in precisely that part of a geosynclinal belt which is characterized by the largely unfossiliferous sediments which seem to have accumulated on the floor of a rapidly sinking oceanic trench. This metamorphism affects the belt as a whole and is something quite independent of the presence of plutonic rocks which are more likely a result than a cause of the metamorphism (Read, 1951, p. 13). It is an all-pervading process of chemical transformation which, as far as it itself is concerned, seems to be also independent of differential movements produced by the orogenic deformation. The question then is: What is it that confines this process to the relatively narrow zones of orogeny?

An answer is suggested by the modern laboratory studies on the synthesis and stability relations of silicates in the presence of water[14]. In England, Lacy has succeeded in synthesizing "certain members of the amphibole family" at 500°C. and 1000 atm. pressure, using rock cylinders of slate, up to nearly a quarter of an inch in diameter, placed into an ingeniously constructed pressure bomb. In another experiment with slate, idioblastic andalusite developed at 760° and above, after 100 hours (Lacy, 1951, p. 538). A team of investigators at the Geophysical Laboratory is attacking on a very broad basis the whole problem of phase-stability relations among silicates in the presence of water vapor. As these studies progress, it is becoming evident that the quantity and pressure of water vapor present in the rock determines most directly what minerals will crystallize, and not temperature and static pressure alone (*i.e.*, depth below the earth's surface) or even differential stress (Yoder, 1951, p. 85).

The belt of geosynclinal sediments must, then, mark a zone where heat and water vapor enter the rock column in a manner not seen elsewhere. To provide access of water vapor

[14] These studies, with their rigid control of temperature and pressure, resume, on the quantitative basis of modern physical chemistry, experiments made a hundred years ago by French investigators, Daubrée especially, whose remarkable qualitative results seem to be all but forgotten.

and heat from below it is necessary to create a zone of deformation across the earth's crust that loosens the rock texture and increases the volume of capillary and subcapillary discontinuities and extend to depths from which water vapor is ready to escape, carrying with it excess heat and ions of dissolved substances. The water vapor in these subcapillary pathways and the water in relatively cooler regions form the medium in which atomic and ionic diffusion can spread through the crystalline fabric of the rock at rates adequate to achieve the results of metamorphism within the available time.

This leads thus to the hypothetical concept that the geosynclinal depressions play a role in the mechanical deformation of the crust comparable to that of a notch in a plate under stress; they localize the appearance of major shear zones and thereby come to lie at the ultimate outlet for the ascending column of water vapor which produces the metamorphism (Bucher, 1950, p. 500; Wegmann, 1935, p. 305–350; 1951, pl 231–237).

The deformation that accompanies the orogenic phases which follow as a result of the crustal shearing proceeds, of course, while the metamorphic changes take place in the rock column. Where deformation is more intense, the agents of metamorphism find quicker access. The greater the squeezing, the higher the metamorphism. But not because a differential pressure is necessary for the formation of the metamorphic minerals; rather because the deformation produced by the differential pressure provides access for the ions needed to form the minerals. Continued strain will produce internal differential movement and may ultimately deform or break individual crystals and the whole crystal fabric, especially when the supply of the substances needed for further changes declines and stops. This gives the word "dynamo-metamorphism" a more adequate meaning than that which connects it with ideas about so-called "stress" minerals.

How far these speculations are justified remains to be seen. They emphasize the dominantly chemical character of the processes that lead to the transformation of sediments into crystalline rocks and they remind us that even the smallest detail we observe may bear somewhere, in some manner, on the most fundamental problems of our science.

Appendix: A Pseudofossil in Gneiss of the Swiss Alps

An example of prolonged argument over a pseudofossil deserves a place here. In 1886, two fragments of what seemed to be treelike stems were discovered accidentally in the gneiss of the northern Swiss Alps, near Guttannen in the Haslital, while a huge block was being split into slabs. The main "stem" is 4¾ feet long and tapers from 6.7 inches to 4.7 inches in width. The strange object that separated so neatly from the gneiss, leaving a sharp impression on the severed face, astonished the workers and caused a local sensation. The director of Public Works sent Edm. de Fellenberg to investigate. Impressed, he sent the whole block to the Museum at Bern.

De Fellenberg and Baltzer reported on the find before the Swiss Society of Natural History in the same year, describing it as a "Carboniferous" tree trunk. Irregularly spaced constrictions suggested a *Calamites*. The find was widely discussed. In his monograph on the Aar Massiv, Baltzer discussed the "stems" further and figured them (Baltzer, 1888, p. 161). He had found no traces of organic matter in the main "stem" and began to doubt its fossil nature.

But most geologists accepted it. Bonney, who would not admit that true crystalline rocks could contain fossils, maintained that the "so-called" gneiss in which the "trunk" had been found was merely a compacted arkose.

When at last the "calamite trunk" was sectioned, it was found that, in contrast to the surrounding micaceous gneiss, it consisted of amphibolite. The well-defined, thin veneer of biotite which had looked so much like the metamorphic equivalent of the thin crust of clayey and organic material that surrounds sandstone molds of tree trunks seen so frequently in Carboniferous strata, needs be nothing more than the biotite rim which quite commonly borders amphibolite layers in mica schists. The thorough paper by Von Fellenberg and Schmidt (1899, p. 81–93), which is well documented with photographs of the specimen and typical cross sections (one even in color), was summed up in a review in the Eclogae Helveticae as follows: "Nothing whatever justifies the claim that these objects are of organic origin.

They are rather inclusions of amphobolite, rolled and laminated in the course of (tectonic) deformation." (Fellenberg and Schmidt, Abstract, p. 411. Translated).

This story has value for two reasons. First, if it appears rather silly to the reader, he had better be on his guard. It shows that at heart he thinks as Judd expressed it in the discussion following Bonney's paper of 1892. Judd said he

"always doubted cases of the alleged occurrence of fossils in holocrystalline rocks. If the rocks are holocrystalline, how could original structures like fossils be preserved? If, on the other hand, the rock did preserve the structure of a fossil, how could it be said to have been perfectly recrystallized?" (Bonney, 1892, p. 399).

We have learned better since then. But we must marshall the courage to refuse to follow our instinctive reactions that hark back to earlier thinking. We must keep alert to the possibility that one day such fossils may be found. Anyone, such as the writer, who has spent much time among the outcrops of Pennsylvanian sandstone in the eastern United States has seen quantities of sand-filled molds of hollow stems standing or lying in a more or less arkosic matrix. As long as metamorphism is essentially a chemical process, such objects will be as surely preserved as the brachiopods in New England gneiss. The fact that one such case proved to be a mistake should not mislead us into casting aside suggestive-looking objects without thorough examination.

The great master of geology, Albert Heim, kept his mind open on the Guttannen "fossil tree trunk". In his *Geology of Switzerland* he points out that it is entirely possible that the "sericite-psammite-gneiss," as he calls the rock in which it was found, is of Carboniferous age and part of the sericite schist zone ("Casanna schists") which not far away contains the well-known conglomerates, black schists, and anthracite. (Heim, 1921, p. 162). Why should such a tree trunk not be found in coal-bearing, coarse clastic sediments?

There is another record of a "fossil tree trunk" in the literature. A very brief note on gneiss with the impression of an *Equisetum*, translated from the original, appeared in the American Journal of Science. It reads as follows:

"The museum at Turin contains a fragment of gneiss from an erratic block, derived apparently from the Valteline (the upper Adda valley in the Italian Alps), from the mass of crystalline rocks of that region which underlie the Infraliassic group of Sismonda. Mr. Sismonda regards the fossil as proof of the metamorphic character of the fundamental gneiss of the Alps. . . ." (Sismonda, 1865, p. 532).

Time did not permit the writer to follow this up. It is probably another "pseudofossil." But it need not be. That is worth remembering.

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fauna drastically, no matter what sediment accumulates on the sea floor. In many dozens of deep-sea cores from the Atlantic and the Caribbean Sea that Maurice Ewing has secured and split open for study, no remains of organisms have been found larger than forams and planktonic pteropods, with one exception. In the distant portion of the submarine canyon of the Hudson River, 180 miles from the shore, and 60 miles[12] beyond the foot of the continental slope, at a depth of 11,382 feet, (3470 m.), numerous fragments of typical shallow-water marine pelecypods and gastropods of still existing species (Pleistocene?), together with pebbles up to half an inch in length, were found intimately mixed with globigerina-rich deep-sea clay. The circumstances point compellingly to a turbidity current, produced by a submarine landslide as the depositing agent (Ericson Ewing, and Heezen, 1952, p. 489; Heezen and Ewing, in press). Kuenen's brilliant application of Daly's concept of turbidity currents to the problems of sedimentation (Kuenen, 1951, p. 14–107; 1952, p. 28–36) is shedding a flood of light on many of the most perplexing problems of geosynclinal[13] sediments; such as, for instance, the association of radiolarites with coarse detrital sediments in the Devonian of the Vosges, mentioned earlier.

As geological information and understanding grow, the concept of an initial geosynclinal stage in the development of an orogenic belt (Bucher, 1933, p. 125–139) appears increasingly justified, a stage in which the geosynclinal floor sinks faster than sediments accumulate. This produces a marine trench of sufficient depth to prevent occupation by a normal marine benthonic fauna and invites the operation of those processes which result in the peculiarities of sedimentation and stratification so generally found in the corresponding portions of geosynclinal sediments.

[12] The figures given are nautical miles. They are, respectively, 207 and 69 statute miles.

[13] Throughout this paper, the writer uses the word "geosyncline" for relatively long and narrow depressions of the earth's crust, the floors of which ultimately sink to depths greatly in excess of the normal depth of the larger basins in which they lie. ("Orthogeosynclines" of Stille and Kay).

Speculations

This brings us back to the crucial fact that regional metamorphism begins and centers in precisely that part of a geosynclinal belt which is characterized by the largely unfossiliferous sediments which seem to have accumulated on the floor of a rapidly sinking oceanic trench. This metamorphism affects the belt as a whole and is something quite independent of the presence of plutonic rocks which are more likely a result than a cause of the metamorphism (Read, 1951, p. 13). It is an all-pervading process of chemical transformation which, as far as it itself is concerned, seems to be also independent of differential movements produced by the orogenic deformation. The question then is: What is it that confines this process to the relatively narrow zones of orogeny?

An answer is suggested by the modern laboratory studies on the synthesis and stability relations of silicates in the presence of water[14]. In England, Lacy has succeeded in synthesizing "certain members of the amphibole family" at 500°C. and 1000 atm. pressure, using rock cylinders of slate, up to nearly a quarter of an inch in diameter, placed into an ingeniously constructed pressure bomb. In another experiment with slate, idioblastic andalusite developed at 760° and above, after 100 hours (Lacy, 1951, p. 538). A team of investigators at the Geophysical Laboratory is attacking on a very broad basis the whole problem of phase-stability relations among silicates in the presence of water vapor. As these studies progress, it is becoming evident that the quantity and pressure of water vapor present in the rock determines most directly what minerals will crystallize, and not temperature and static pressure alone (*i.e.*, depth below the earth's surface) or even differential stress (Yoder, 1951, p. 85).

The belt of geosynclinal sediments must, then, mark a zone where heat and water vapor enter the rock column in a manner not seen elsewhere. To provide access of water vapor

[14] These studies, with their rigid control of temperature and pressure, resume, on the quantitative basis of modern physical chemistry, experiments made a hundred years ago by French investigators, Daubrée especially, whose remarkable qualitative results seem to be all but forgotten.

and heat from below it is necessary to create a zone of deformation across the earth's crust that loosens the rock texture and increases the volume of capillary and subcapillary discontinuities and extend to depths from which water vapor is ready to escape, carrying with it excess heat and ions of dissolved substances. The water vapor in these subcapillary pathways and the water in relatively cooler regions form the medium in which atomic and ionic diffusion can spread through the crystalline fabric of the rock at rates adequate to achieve the results of metamorphism within the available time.

This leads thus to the hypothetical concept that the geosynclinal depressions play a role in the mechanical deformation of the crust comparable to that of a notch in a plate under stress; they localize the appearance of major shear zones and thereby come to lie at the ultimate outlet for the ascending column of water vapor which produces the metamorphism (Bucher, 1950, p. 500; Wegmann, 1935, p. 305–350; 1951, pl 231–237).

The deformation that accompanies the orogenic phases which follow as a result of the crustal shearing proceeds, of course, while the metamorphic changes take place in the rock column. Where deformation is more intense, the agents of metamorphism find quicker access. The greater the squeezing, the higher the metamorphism. But not because a differential pressure is necessary for the formation of the metamorphic minerals; rather because the deformation produced by the differential pressure provides access for the ions needed to form the minerals. Continued strain will produce internal differential movement and may ultimately deform or break individual crystals and the whole crystal fabric, especially when the supply of the substances needed for further changes declines and stops. This gives the word "dynamo-metamorphism" a more adequate meaning than that which connects it with ideas about so-called "stress" minerals.

How far these speculations are justified remains to be seen. They emphasize the dominantly chemical character of the processes that lead to the transformation of sediments into crystalline rocks and they remind us that even the smallest detail we observe may bear somewhere, in some manner, on the most fundamental problems of our science.

Appendix: A Pseudofossil in Gneiss of the Swiss Alps

An example of prolonged argument over a pseudofossil deserves a place here. In 1886, two fragments of what seemed to be treelike stems were discovered accidentally in the gneiss of the northern Swiss Alps, near Guttannen in the Haslital, while a huge block was being split into slabs. The main "stem" is 4¾ feet long and tapers from 6.7 inches to 4.7 inches in width. The strange object that separated so neatly from the gneiss, leaving a sharp impression on the severed face, astonished the workers and caused a local sensation. The director of Public Works sent Edm. de Fellenberg to investigate. Impressed, he sent the whole block to the Museum at Bern.

De Fellenberg and Baltzer reported on the find before the Swiss Society of Natural History in the same year, describing it as a "Carboniferous" tree trunk. Irregularly spaced constrictions suggested a *Calamites*. The find was widely discussed. In his monograph on the Aar Massiv, Baltzer discussed the "stems" further and figured them (Baltzer, 1888, p. 161). He had found no traces of organic matter in the main "stem" and began to doubt its fossil nature.

But most geologists accepted it. Bonney, who would not admit that true crystalline rocks could contain fossils, maintained that the "so-called" gneiss in which the "trunk" had been found was merely a compacted arkose.

When at last the "calamite trunk" was sectioned, it was found that, in contrast to the surrounding micaceous gneiss, it consisted of amphibolite. The well-defined, thin veneer of biotite which had looked so much like the metamorphic equivalent of the thin crust of clayey and organic material that surrounds sandstone molds of tree trunks seen so frequently in Carboniferous strata, needs be nothing more than the biotite rim which quite commonly borders amphibolite layers in mica schists. The thorough paper by Von Fellenberg and Schmidt (1899, p. 81–93), which is well documented with photographs of the specimen and typical cross sections (one even in color), was summed up in a review in the Eclogae Helveticae as follows: "Nothing whatever justifies the claim that these objects are of organic origin.

They are rather inclusions of amphobolite, rolled and laminated in the course of (tectonic) deformation." (Fellenberg and Schmidt, Abstract, p. 411. Translated).

This story has value for two reasons. First, if it appears rather silly to the reader, he had better be on his guard. It shows that at heart he thinks as Judd expressed it in the discussion following Bonney's paper of 1892. Judd said he

"always doubted cases of the alleged occurrence of fossils in holocrystalline rocks. If the rocks are holocrystalline, how could original structures like fossils be preserved? If, on the other hand, the rock did preserve the structure of a fossil, how could it be said to have been perfectly recrystallized?" (Bonney, 1892, p. 399).

We have learned better since then. But we must marshall the courage to refuse to follow our instinctive reactions that hark back to earlier thinking. We must keep alert to the possibility that one day such fossils may be found. Anyone, such as the writer, who has spent much time among the outcrops of Pennsylvanian sandstone in the eastern United States has seen quantities of sand-filled molds of hollow stems standing or lying in a more or less arkosic matrix. As long as metamorphism is essentially a chemical process, such objects will be as surely preserved as the brachiopods in New England gneiss. The fact that one such case proved to be a mistake should not mislead us into casting aside suggestive-looking objects without thorough examination.

The great master of geology, Albert Heim, kept his mind open on the Guttannen "fossil tree trunk". In his *Geology of Switzerland* he points out that it is entirely possible that the "sericite-psammite-gneiss," as he calls the rock in which it was found, is of Carboniferous age and part of the sericite schist zone ("Casanna schists") which not far away contains the well-known conglomerates, black schists, and anthracite. (Heim, 1921, p. 162). Why should such a tree trunk not be found in coal-bearing, coarse clastic sediments?

There is another record of a "fossil tree trunk" in the literature. A very brief note on gneiss with the impression of an *Equisetum*, translated from the original, appeared in the American Journal of Science. It reads as follows:

"The museum at Turin contains a fragment of gneiss from an erratic block, derived apparently from the Valteline (the upper Adda valley in the Italian Alps), from the mass of crystalline rocks of that region which underlie the Infraliassic group of Sismonda. Mr. Sismonda regards the fossil as proof of the metamorphic character of the fundamental gneiss of the Alps. . . ." (Sismonda, 1865, p. 532).

Time did not permit the writer to follow this up. It is probably another "pseudofossil." But it need not be. That is worth remembering.

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NONRADIOGENIC ISOTOPES IN GEOLOGY: A REVIEW

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PART I. SUMMARY OF RESULTS TO DATE

Introduction

General Statement

The study of the abundance and distribution of isotopes is in an explosive phase. In the few years that have elapsed since the first interpretations were made by this new method thousands of determinations have been reported in hundreds of published papers. Acceleration continues, and, before the subject becomes too complex and cluttered with data, it is appropriate to summarize what has been accomplished and to suggest certain paths that might profitably be taken in the near future.

Before the actual data are summarized, however, it will be worthwhile to discuss some ideas, general principles, and cautions that bear on the subject.

Atomic Weights

The whole problem of atomic weights is now closely bound to the concept of isotopic constitution of the elements. The scale of *physical atomic weights* is based on $O^{16} = 16.0000$ and

so is independent of the source of the oxygen. The value for atomic weights of polyisotopic elements, however, may vary with the source of the elements even on this scale.

On the scale of *chemical atomic weights* the base itself is variable, because it takes "normal" oxygen = 16.0000, but the textbooks and tables do not define *normal oxygen* as to source or isotopic composition. Most textbooks of physical and inorganic chemistry give the chemical atomic weight of oxygen as 16.0044 on the physical scale, which gives a conversion factor of 1.000275 between the two scales. A few recent text-books, e.g., Emeléus and Anderson (1952, p. 32–33), point out that the value of the conversion factor depends on the ratio O^{16}/O^{18} for "normal" oxygen, but they still do not indicate that this ratio varies significantly for materials with different geologic, or biologic, histories.

Twenty-five years ago, and much more recently in many schools, students of chemistry and physics were taught that, in general, elements have constant atomic weights. Some exceptions, such as lead, were recognized, where one or more isotopes are the end members of radioactive series, but the other elements were considered to be of constant isotopic composition regardless of the geological or biological processes they had undergone in nature.

This idea is in part responsible for the development of methods for more accurate atomic-weight determinations, because, if it were true, atomic weights would be independent of the source of the elements and would be constant to as many places as they could be measured. The fact that this concept is not strictly true is no doubt responsible for some of the discrepancies in atomic-weight values.

In the future, determinations of atomic weights should be tied closely to studies of isotopic composition and variations thereof. Values of atomic weights should not be given to more places than is warranted by the known isotopic variation in nature. Perhaps they should be recorded with a "plus or minus" factor to indicate the known variability for elements that have been studied sufficiently isotopically.

Standards for Isotope Determinations

Standards are available for reference in chemical atomic-weight determinations. It is even more important that standards be available for isotope studies, because atomic weights depend upon isotopic composition. Modern instrumentation makes it possible to determine isotopic composition of most elements very accurately, and it would be comparatively simple to set up a series of standards. They would be extremely useful for atomic-weight work as well as for checking instrumental techniques, for comparing instruments, and for providing a common denominator for reporting results of isotope studies so that the data of one worker or group of workers could be compared directly with those of any other.

The present method of reporting results is highly unsatisfactory. Each institution selects a convenient standard with reference to which a series of results is reported. They may use a quite different standard for reporting another series. In some papers the isotopic composition of the standard is not given, so the results are useful only for comparisons of materials reported in that particular paper. Individuals or groups at the same institution use different standards and different methods of reporting results. Different laboratories rarely use standards that are closely comparable and never use identical ones.

If, say, the Bureau of Standards could serve as a clearing house of information on standards, and perhaps as a repository and distributor of standards, it would be a great service not only to workers in isotope geology but also to everyone interested in abundance of isotopes.

Several inaccuracies have been printed that probably would have been caught and corrected had standards been available. There are undoubtedly others still undetected.

Good standards, properly used, would assure early detection of faulty techniques and instrumentation and would allow comparison of results obtained with different equipment.

Other Information Needed; Assumptions

There are other sources of inaccuracies and inadequacies, however, that cannot be remedied, or even detected, in this manner. *Proper*

sampling is as much a problem in studies of isotopes as it is in ordinary chemical and spectrographic analyses. Failure to specify accurately the *source of material* can make the results valueless for many purposes, and especially for making geologic interpretations. For some types of problems it will not be sufficient to determine the isotopic composition of an element in a rock, or even of mineral fractions from a rock; analyses will have to be made on the material from different zones or parts of individual crystals. Failure to recognize the isotopic variability of another element combined with the one being studied can, and in many instances has, completely invalidated the results.

For many geological interpretations based on the distribution of isotopes, information is needed which is not immediately or directly available. In the laboratory it is comparatively simple to measure the factors involved—isotopic composition of original materials and products, temperature, rate of diffusion, distances, time, etc.—and to relate them to one another as desired for the specific purpose. In nature, however, it may not be possible to determine any factors except the present isotopic composition of the material, which may be the result of a reaction or process that took place half a billion or more years ago. The interpretation, then, becomes a game that involves evaluating by independent means the other factors essential to the solution of the problem—extrapolation, deduction, measurement of other properties of the material or associated substances, or just making assumptions, the accuracy of which varies tremendously according to the circumstances of the problem.

In studying geological material the first assumption is that the isotopic composition of the specimen has not changed since the conclusion of the process of formation or alteration in which we are interested. This assumption can be substantiated in varying degrees; sometimes it can be disproved by showing that the material is undergoing exchange that will affect its isotopic composition in the environment in which it was collected. Many times the assumption appears to be valid on general grounds, but only rarely is it possible to prove that no adverse exchange has taken place. Specific examples in which exchange has probably been operative and others in which it is probably not significant are discussed below under the individual elements.

In certain types of problems, such as those involving products of chemical exchange reactions, it is necessary to assume further that the isotopic composition of the solution, or other medium from which the material formed, had the same isotopic composition that similar media have today, or that its isotopic composition can be estimated. As we study more ancient materials, more fundamental questions are brought up, such as, "Did water and dissolved salts of the Precambrian sea have the same isotopic composition as those of the modern oceans? Did ancient organisms have more, or less, power to take up isotopes selectively than do their modern counterparts? What was the isotopic composition of the various elements in the original (molten?) earth? Was isotopic composition uniform throughout the primitive earth? If not, how did it vary? If so, when and how did the first fractionation take place? Is the average isotopic composition of the earth the same as that of the solar system? Is the cosmic abundance of nuclear species about the same as that in the solar system?"

The more exact answers we get to such questions, largely through more and better isotope determinations, the more certain will isotope interpretations become, especially those concerned with very old materials. Some of them can already be answered with a fair degree of certainty, at least for certain elements. For example, oxygen appears to have essentially the same isotopic composition in basic rocks of all ages and in meteorites. Presumably, then, this ratio is essentially that of the primitive earth and possibly of the whole solar system. There is increasing evidence that the same may be true for iron, gallium, sulfur, and other elements. On theoretical grounds there is very little chance that there could be any fractionation of isotopes at temperatures at which the earth would be molten. Fractionation or nonfractionation of isotopes by extinct organisms can only be inferred by analogy with similar modern species, unless a certain group or species always prefers a certain isotope, regardless of geological environment. Very little is known of the cosmic abundance of isotopes, but it has been shown that the isotopic composition of

carbon varies greatly in the atmospheres of different types of stars. It is logical that other light elements may show similar variations. Measurements made on stars are unlikely to reflect cosmic abundance very accurately because (Brown, 1949):

1. There is still considerable difficulty and uncertainty in converting spectral intensities to atomic abundances.
2. There is much uncertainty as to whether or not elements are homogeneously distributed throughout stellar interiors.

The first of these difficulties is the principal one insofar as isotopic abundances are concerned; even in the laboratory, where source material, as well as other factors, is subject to close control, it is difficult to convert spectral intensities to isotopic abundances. When one is analyzing the faint light from a distant star, the difficulties are increased many times.

The second uncertainty may not apply to isotopes directly. Almost certainly there is no fractionation of isotopes at stellar temperatures. Possibly, however, at the temperatures and pressures obtaining in the far interiors of some types of stars, isotopes are forming that are not being produced at or near the surfaces of these stars. This is not isotopic fractionation, but it can produce the same effect if rates of formation of the isotopes and of exchange of material between interior and exterior of the stars are such that a gradation in the concentrations of those isotopes is maintained between interior and exterior.

Inhomogeneity in distribution of an element in a star may make determination of its isotopic constitution difficult, even though its composition is uniform. For example, a very dense element may be abundant in a stellar interior and rare in the atmosphere of the star. Intensity of spectral lines of an element varies with its concentration, so in the above example it may be difficult, or impossible, by existing techniques to determine the isotopic composition of the element concerned, whereas it might possibly be done if the spectrum of the interior of the star could be obtained.

Estimates of Abundance

Brown (1949) has summarized knowledge of the abundances of the elements in stars, in meteorites, and in the sun. He points out that approximate isotopic identity between meteorites and terrestrial material has been established for about a dozen elements. With this assumption and the available information on relative abundance of the elements in meteorites and the isotopic composition of terrestrial matter, he compiles a broader table of nuclear abundances than was available before. Urey (1952a, p. 231–233; 1952b, p. 252) has revised Brown's figures.

Seaborg and Pearlman (1948) and more recently Bainbridge and Nier (1950) have compiled excellent tables of relative isotopic abundances of the elements, and bibliographies of the work in which they were established. Nier (1952) has brought the summary more nearly up to date by publishing a review of the papers on isotopic abundance which appeared in 1950.

There have also been many attempts to account for relative abundance and distribution of the elements and their isotopes. Alpher and Herman (1950, p. 208–212) have given an excellent summary and bibliography of this subject.

Most of the experimental work on which these compilations of terrestrial abundances are based assumed that isotopic composition is independent of the source of the material. Indeed, much of the work was an attempt to obtain more accurate values for the atomic weights of various elements. Source material, therefore, was commonly from purified reagent chemicals, and little or no attention was paid to the geologic, or biologic, environment or history of the original minerals, or other compounds, from which the various elements were derived.

There is now a growing realization that at least many polyisotopic elements undergo isotopic fractionation in nature. This fractionation is no doubt responsible for some of the observed differences in isotopic composition and consequent differences in average atomic weights obtained by different workers, although many are probably due to differences in techniques and instrumentation, which would give different results on the same sample.

Although isotopic abundances have been determined for all the elements that have more than one isotope, comparatively few studies have been made of isotopic variations in nature. Summaries of earlier work have appeared:

(Goodman, 1942, p. 285–288; Kamen, 1946; Thode, 1949). These were by no means complete when they appeared and are now badly out of date. Marble (1952) has compiled a more lengthy bibliography, including work on radioactive and radiogenic isotopes, as well as isotopes not known to be either radioactive or the products of radioactive disintegrations. He sums up principles, general results, and conclusions succinctly without giving details of the results reported in individual papers.

Scope of this Review

The following summary attempts to give a complete account of the significant work that has been done on fractionation in nature of isotopes whose present relative abundance cannot have been affected by production or disintegration of radioactive isotopes. Thus lead is not considered because the present isotopic composition of a given sample is determined by the amount of common lead it contains, its age, and the relative amounts of thorium, U^{235}, and U^{238} present at the time of its formation, rather than by any physical or chemical processes of fractionation. Neither is C^{14} considered, because it is constantly being produced by cosmic-ray bombardment.

On the other hand, isotope pairs like K^{39}/K^{40} where one isotope is radioactive, or U^{238}/U^{235} where both are radioactive, are considered, because the present ratio will be the same regardless of the age or source of a sample, unless partial separation has been brought about by some physical or chemical process of fractionation that would have operated without regard to the radioactivity of the isotopes. He^4/He^3 is considered briefly. There is uncertainty regarding the origin of He^3, but whatever its source there are certain situations in which fractionation by diffusion can produce a change in the ratio and thus provide a chance for geologic interpretations. Pairs of light stable isotopes not related to radioactive series, like C^{12}/C^{13} and O^{16}/O^{18}, receive the bulk of consideration.

The reports of the Committee on the Measurement of Geologic Time of the National Research Council give complete coverage of the work done on radioactive isotopes and the end members of their respective series. These reports are of much broader scope than the present summary, as they cover physical, chemical, and spectrographic methods of analysis, other laboratory techniques for studying radioactivity and radioactive minerals, descriptions of radioactive minerals and their occurrences, synthesis of radioactive minerals, structures of radioactive minerals, and many other subjects related only indirectly, if at all, to the application of isotopic abundance to geologic problems.

These reports serve a very useful purpose, but they are too inclusive to provide convenient reference for the subject under discussion. It probably would be worth while to summarize the work done on studies of abundance and distribution of radioactive and radioactive-derived isotopes, where the fractionation has been produced by radioactive disintegration, and the geologic interpretations that have been made, or might be made, thereby.

Some of the papers not summarized in the text are annotated briefly in the bibliography.

Hydrogen

General Remarks

Because of the very considerable interest in heavy water many papers have appeared in recent years on the occurrence and separation of deuterium, the properties of its compounds, and related subjects. A complete summary of the literature to 1949 is given by Kimball (1949). This book lists 122 papers dealing with the abundance of deuterium. Kirshenbaum (1951, p. 376–427) has a chapter of 52 pages, with a bibliography of 60 titles, on the natural abundance of hydrogen and oxygen isotopes.

Much of the early work on heavy hydrogen was done by merely measuring the density of water (natural, or prepared from the hydrogen being studied) accurately and assuming that variations in the density were due entirely to variations in the H^1/H^2 ratio. It is now known that the O^{16}/O^{18} ratio varies appreciably in water and other hydrogen-containing compounds, so most of that early work is of relatively little value now for interpretations of the abundance of hydrogen isotopes. Where systematic differences in density have been established for natural waters for which localities, environment, etc., are known, however,

attention should be called to the results even though it is not yet known how much of the anomaly is due to variations in H^1/H^2 and how much to O^{16}/O^{18}. This will point out promising areas in which further studies of the separate ratios may make more detailed and accurate interpretations possible.

It is not practicable to discuss, or even to list, in a review of this kind all the work that has been done on variations of the H^1/H^2 ratio in nature. The papers mentioned have been selected to illustrate principles, to summarize the seemingly best estimates of natural abundance of deuterium and hydrogen, and to point up geological problems.

In 1933 Lewis discussed reactions of the type $H^1H^2O + NH_3^1 \rightleftarrows H_2^1O + NH_3^1H^2$ and performed qualitative experiments that demonstrated the reality of such isotopic exchanges. He did not evaluate the factors quantitatively, but concluded that the work showed "that with refinement we shall have an exact method for analyzing water containing isotopes of both oxygen and hydrogen."

Wahl and Urey (1935) gave values for the vapor pressures of HDO^{16}, H_2O^{16}, D_2O^{16}, and H_2O^{18} at various temperatures[1]. They concluded that "the isotopes of hydrogen can probably be separated by fractional distillation (of water), but separation of the isotopes of oxygen (by this method) will be considerably more difficult." Urey, Pegram, and Huffman (1936) reported on results with a fractionating column 6 inches in diameter and 35 feet high, with 619 rotating and an equal number of stationary cones, which is equivalent to 230 theoretical plates. After supplying 50 cc. of water per minute for 8 days they observed a threefold increase of O^{18} and a fortyfold increase of H^2. With total reflux, water with less than the original content of O^{18} was produced at the top of the tower.

Relation between Density and Isotopic Composition of Water

Washburn, Smith, and Frandsen (1933) have given formulas relating density and isotopic composition of water. The simplified equation for the effect of deuterium[2] is

$$P_2 = 8.957\,\Delta + 0.00003$$

where P_2 = atomic fraction of H^2 and Δ = difference in density (in γ)[3] between the sample being studied and ordinary water, assuming the oxygen content of the sample to be isotopically normal.

In 1933 the accepted value of H^1/H^2 was around 30,000, which is reflected in the constant, 0.00003, of the equation. It now appears that the value of H^1/H^2 is ca. 6700, so the constant should be about 0.00015. The revised equation, then, is

$$P_2 = 8.957\,\Delta + 0.00015$$

Work on the isotopes of hydrogen has been reported chiefly in terms of deviation of the density of water formed by combination of a hydrogen sample with normal oxygen from the density of normal water, and directly as the ratio H^1/H^2. For comparisons of results reported by these methods it will be convenient to have a graph relating them. Accordingly, values of H^1/H^2 have been calculated by the equation as modified above for values of Δ from $+8$ to -5γ and are plotted in Figure 1.

Lewis and Luten (1933) give two equations from which the complete isotopic composition (neglecting O^{17}) can be calculated for water whose density and index of refraction have been determined:

$$x = 1.370\,\Delta S - 190.5\,\Delta n$$
$$y = 7.692\,\Delta S + 180.9\,\Delta n$$

where x and y are the increases in mole fractions of H_2^2O and H_2O^{18}, respectively, over the corresponding values in ordinary water and ΔS and Δn are the differences (at 25°C) between the density and index of refraction, respectively, of a given sample and the corresponding values for ordinary water.

Normal Terrestrial Abundance of Hydrogen Isotopes

Many estimates of the relative abundance of H^1 and H^2 in terrestrial materials have been

[1] D = H^2. These symbols are used interchangeably; the usages of the individual authors have been followed.

[2] *See* the section on Oxygen for the equation for the effect of O^{18}.

[3] $1\gamma = 1 \times 10^{-6}$ d (d = density of water at 3.98°C.)

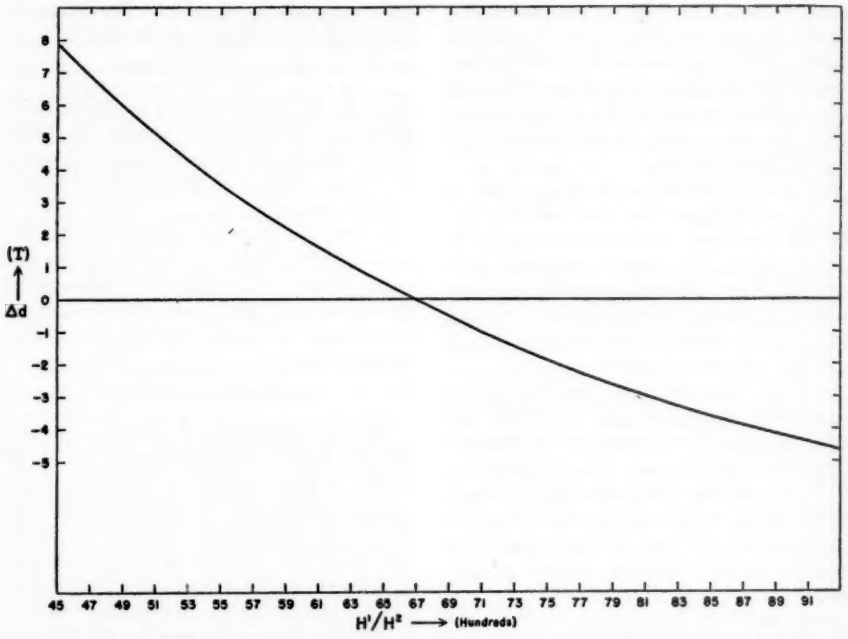


FIGURE 1.—GRAPH SHOWING RELATION BETWEEN H^1/H^2 AND THE DIFFERENCE IN DENSITY BETWEEN NORMAL WATER AND WATER PREPARED BY COMBINING A GIVEN SAMPLE OF HYDROGEN WITH OXYGEN OF NORMAL ISOTOPIC COMPOSITION

TABLE 1.—TERRESTRIAL ABUNDANCE OF HYDROGEN AND DEUTERIUM

Reference	Source of water	H^1/H^2
Lewis and Macdonald (1933, p. 344)	Berkeley, California	6500
Edwards, Bell and Wolfenden (1935, p. 793)	Oxford, England	6220 ± 300
Hall and Jones (1936, p. 1919)	Lake Mendota, Wisconsin	6400 ± 200
Gabbard and Dole (1937, p. 185)	Lake Michigan	6900
Morita and Titani (1938c, p. 423)	Cambridge, Massachusetts	6200 ± 200
	Osaka, Japan	
Tronstad and Brun (1938, p. 772)	Rain and snow	5960 ± 300
	Mosvann, Norway	
Voskuyl (Thesis, Harvard University, 1938)	Cambridge, Massachusetts	6700 ± 50
	London tap water	
	Osaka, Japan	
Swartout and Dole (1939, p. 2029)	Lake Michigan	6970
	Atlantic Ocean	6900

made. Most of the early values for H^1/H^2 were far above the one accepted today, and source of the water was not indicated in most of the papers. Bainbridge and Nier (1950) accept 6700 as the best value of H^1/H^2. They list 17 determinations made from 1933 to 1939 for which the average is about 6500. The best available results for which source of sample is given are listed in Table 1.

Data on localities and sampling are not given in detail, but there are enough results by a number of workers to show that H^1/H^2 for

normal surface waters is probably close to 6,500 and almost certainly lies between 5,900 and 6,900.

Taylor (1934) mentions a report by Bleakney and Gould that, for ordinary water, $H^1/H^2 > 5 \times 10^8$ and, for D_2O, $D/H^2 > 5 \times 10^4$.

TABLE 2.—VARIATIONS IN DENSITY OF WATER FROM VARIOUS SOURCES (Riesenfeld and Chang, 1936c)

Occurrence	Δd (γ)
Snow	−2.3
Rain	−1.0
Land water	0.0
Animals	+1.2
Oceans	+1.5
Plants	+1.7
Minerals	+2.4

Grosse, Johnston, Wolfgang, and Libby (1951) determined the H^2 content of some heavy water that had been produced in Norway. From the ages of the samples and assumed separation factors for the process utilized in preparing the heavy water, they estimate the natural abundance of H^2 in Norwegian surface waters is of the order of 1×10^{-18}; *i.e.*, $H^1/H^2 \sim 10^{18}$. There is considerable uncertainty as to the value of the separation factors, so the estimate is probably not accurate within a factor of 10. These values show that in ordinary measurements of the isotopic composition of hydrogen H^2 need not be considered. Because of its radioactivity, however, it can be determined with sufficient accuracy so that studies of its abundance might help solve some geologic problems. (*See* Part II.)

Riesenfeld and Chang (1936b) report that "normal" water (ground and river water, etc.) contains 0.035% HDO and 0.2% H_2O^{18}, corresponding to density differences of 18.3γ and 220γ, respectively. Ocean water shows an average excess density over fresh water of 1.5γ. Ocean water contains 0.036% HDO, corresponding to $\Delta d = 18.9\gamma$, so $18.9\gamma - 18.3\gamma = 0.6\gamma$ of the excess density must be due to increased H^2 in sea water, and the remaining 0.9γ to O^{18}.

These values for river, lake, and ocean waters are in a way averages of water from many sources. They may be taken as the norm for studies of variation in water from simpler sources. But for very accurate determinations the source and composition of the standard water must be defined more closely, because studies have shown significant variation in isotopic composition among river, lake, and sea water and even among different places in the same river. (*See also* section on Oxygen.)

TABLE 3.—DENSITY OF WATER OF HYDRATION IN MINERALS (Riesenfeld and Tobiank, 1935)

Mineral and locality	Δd
Kernite (Rasorite), $Na_2B_4O_7 \cdot 4H_2O$, California	+6.3γ
Tincal, $Na_2B_4O_7 \cdot 10H_2O$, California	+2.73
Carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$, Stassfurt	+3.36
Polyhalite, $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$, Stassfurt	+0.04
Gypsum, $CaSO_4 \cdot 2H_2O$, Südharz	+0.034

For example, Riesenfeld and Chang (1936c) measured the density of water from various sources and compared these densities with that of standard "land water" (Table 2).

These differences are readily explained by more rapid evaporation of the lighter molecules and their easier escape from plant and animal tissues by diffusion and evaporation.

Cosmic Abundance of Hydrogen Isotopes

Taylor (1934) reports an estimate by Menzel at Harvard from astronomical spectrograms that the cosmic value of $H^1/H^2 > 5 \times 10^5$, which indicates a tremendous loss of H^1 during the formation and early history of the earth. Claas (1951) obtained a still larger value for this ratio—$>4 \times 10^7$.

Hydrogen Isotopes in Water of Hydration

The explanation of the greater density of water of hydration of minerals is that they crystallized from supersaturated solutions in which heavy water had been concentrated by evaporation. The minerals studied were evaporites. An earlier article (Riesenfeld and Tobiank, 1935) gives results for individual minerals (Table 3).

In this and still earlier work (Riesenfeld and Riesenfeld, 1934) it had been expected that water of crystallization in minerals would be considerably heavier than was actually found.

This prediction was based on the finding by Taylor, Caley, and Eyring (1933) that NaCl and $BaCl_2$ are 15% and 19% less soluble in D_2O than in H_2O. Shearman and Menzies minerals crystallized from concentrated solutions (evaporites). For example, carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$, gave water with 0.233, 0.298, and 0.412% H_2^2O. These concentrations are

TABLE 4.—DENSITY OF WATER FROM METAMORPHIC MINERALS AND ROCKS (Verdnasky, Vinogradov, and Teis, 1941, p. 575)

Material	Locality	Age	T°C*	% H_2O	Δd_γ
Chlorite schist	Kosmodemyansk, Urals	Devonian?	860	—	+8.6
Chlorite schist	Southern Chibiny Tundras	Precambrian	1,140	4.1	+14.4
Sericite-chlorite-epidote schist	Mt. Mishenaya, Petropavlosk, Kamchatka	Mesozoic	860	—	+12.0
Talc-chlorite schist	Segozero, Karelia	Precambrian	1,140	4.8	+10.6
Talc-chlorite schist	Inguletz River, near Skalevatki, Ukranian Krivoroje	Precambrian	1,140	7.3	+10.7
Talc	Shabrov, Urals	Precambrian	1,140	3.0	+11.0
Serpentine (Williamsite)	Pennsylvania	Precambrian	860	11.4	+6.1
Serpentine	Bajenov, Urals	Precambrian	860	—	0.0
Ophite	Bajenov, Urals	Precambrian	860	11.4	+0.7

* Temperature at which water was driven off.
Maximum error of measurement, $\pm 0.3\gamma$.

TABLE 5.—DENSITY DIFFERENCES DUE TO D AND O^{18} IN WATER FROM TALC-CHLORITE SCHIST (Verdnasky, Vinogradov, and Teis, 1941, p. 576)

Material	Locality	Δd_s	Δd_D	$\Delta d_{O^{18}}$
Talc-chlorite schist	Segozero, Karelia	10.6	−1.2	+11.8
Talc-chlorite schist	Inguletz River, Krivoroje	10.7	−2.9	+13.6

(1937) found that KCl is 16% less soluble in D_2O than in H_2O at 0°C. At 180°, however, the difference is reduced to 4%. The findings for minerals are explained by assuming that the rate of crystal growth is slow compared to the exchange rate of D_2O between the liquid and crystalline phases.

Washburn and Smith (1934a) found the water of hydration from kernite to be 7γ heavier than normal water.

Briscoe, in a discussion of his work with Emeléus and others (*see* Emeléus *et al.*, 1934, discussion, p. 491), reports that water of hydration of mineral salts is 3.0 to 7.5γ heavier than normal water, but he does not name the salts or say whether they are minerals or merely inorganic salts.

Bruni and Strada (1934) reported a considerable concentration of heavy water in hydrous much higher than those measured by other workers. Determinations of separation of isotopes of water by fractional crystallization reported by Bruni and Strada in this same paper had to be corrected later (*see* below), so the results on water from carnallite may be in error also.

Anderson *et al.* (1937, p. 1498) report water from muscovite from Tanganyika to be 0.8γ heavier than normal water; that of a muscovite from Nellore district, Madras, India, 3.4γ heavier; experimental error, $\pm 0.2\gamma$.

Vernadsky, Vinogradov, and Teis (1941) give results of density determinations on water from several metamorphic minerals and rocks (Table 4). They did more detailed work on two of the samples, to determine what part of the density increase was due to O^{18} (Table 5). The increase in density is due entirely to O^{18}, since

H^2 is less abundant in the water from the minerals than in normal water.

Erlenmeyer and Gärtner (1934) confirmed experimentally the interpretation by Riesenfeld and his coworkers that the heavier water in hydrous minerals is there because of concentration in the solution by evaporation. They found:

(1) Equal division of light and heavy water in hydrous crystals of sodium sulfate and the solution from which it was crystallizing.

(2) No preferential interchange of the isotopes of hydrogen between crystals of KH_2PO_4 and its saturated solution.

In the discussion by Briscoe (Emeléus, *et al.*, 1934, p. 492) it is noted that Hughes, Wilson, and Day confirmed these results much more impressively by crystallizing salts, including sulfates and carbonates, from water 2,000 ppm heavier than normal water and comparing the density of the water of hydration of the crystals with that of the water of the solution. They found the densities to be the same within 1 ppm, which showed that any fractionation of isotopes was less than 0.1%.

Both Briscoe and Erlenmeyer and Gärtner, however, measured only the density of *all* the water from a given hydrate. Anderson *et al.* (1937) performed an interesting series of experiments indicating that isotopic fractionation may take place as the water of hydration is driven off. They dehydrated $CuSO_4 \cdot 5H_2O$ completely and then rehydrated it with water containing 0.5% D_2O. Then, in three batches, the water was driven off in two steps, 4 moles first, and then the fifth mole collected and measured separately. In each case, heavier water came off first, contrary to expectation. The difference was greater when the dehydration was performed *in vacuo*.

In a second series of experiments, 1 mole of water containing 0.5% D_2O was added, then 4 moles of normal water. Stepwise dehydration produced the same results as before. The authors conclude that the lighter water is held preferentially by the salt rather than that the heavier water is expelled preferentially from it; also, that no quantitative significance can yet be attached to the results.

Vernadsky, Vinogradov, and Teis (1941, p. 576) found a similar fractionation when they expelled water from chlorites—"density of the water of the first fractions (500–600°) was somewhat higher compared to that of the following ones, obtained at a higher temperature (1140°)."

Fractionation by Evaporation; Isotopic Composition of Sea Water

Tucholski (1934) suggested that the rate of evaporation is important in determining the amount of concentration of heavy isotopes. He found that a 600 cc residue from 25 l. of distilled water that had evaporated slowly from a bottle had a density of 1.0016 at 4°C, whereas a residue obtained by boiling away that same percentage of distilled water had a density of only 1.0001. He ventures the opinion that, in mountain caves where evaporation is slow, a higher percentage of heavy water is likely to be found than in bodies of water with large surface areas where evaporation is intense.

It has been repeatedly demonstrated, however, that the heavy isotopes are concentrated in sea water with respect to river or lake water. Wirth, Thompson, and Utterback (1935) made a fairly extensive investigation of the density of sea water from various locations and at different depths. Their apparatus was sensitive to density differences of the order of 1×10^{-6} (0.01γ). Water distilled from samples from the Mediterranean Sea, Red Sea, and Indian Ocean ranged from $+1.30\gamma$ to $+1.39\gamma$ with respect to water distilled from (Seattle, Wash.) tap water. One sample from a depth of 4000 m in the Indian Ocean gave an anomalous result of $+1.67\gamma$. No surface sample was available at this point, and no explanation of the anomaly is offered.

Samples from the Antarctic Ocean, North Pacific Ocean (51°+ N), and Bering Sea gave lower results; seven samples averaged $+1.17\gamma$. Very low values for the Baltic (0.21, 0.33, and 0.53γ) are attributed to dilution by fresh water, which is also indicated by the low chlorinities of the samples.

At one station, 90 miles west of Cape Flattery (48°18.5′ N.; 127°05′ W.), samples were collected from the surface to a depth of 2000 m. Chlorinity increased from 17.5 g/kg at the surface to 19.2 at 1400 m, below which it remained constant. The density values do not change

progressively, however, but fall apparently into four groups:

(1) 0–50 m $\Delta d = +1.54\gamma$
(2) 100–600 m $\Delta d = +1.29\gamma$
(3) 800–1,800 m $\Delta d = +1.63\gamma$
(4) 2000 m $\Delta d = +1.12\gamma$

These zones correspond in general to those of dissolved oxygen reported by Thompson, Thomas, and Barnes (1934); regions of high oxygen correspond to those of low density and *vice versa*. Rakestraw, Rudd, and Dole (1951) found a marked correlation between the rise of the O^{18}/O^{16} value and the decline with depth in percentage of oxygen dissolved in Pacific Ocean water. The O_2 content and O^{18}/O^{16} ratio show a minimum (about 7% as much dissolved O_2 as at the surface) and maximum (O^{18} sample $- O^{18}$ air $= +0.0063$), respectively, at about 700 m. They concluded that marine organisms that consume dissolved oxygen metabolize O^{16} preferentially.

Several samples from East Sound, San Juan Archipelago, were measured and found to be only 0.8γ above tap water. Chlorinity is 16.1, so there is not nearly enough dilution with fresh water to explain the low density. Marine flora and fauna are unusually abundant in the Sound; Wirth, Thompson, and Utterback (1935) suggest that there may be a relation between biological processes and density differences. This hypothesis may find support in the finding (Lewis, 1933; Taylor, Swingle, Eyring, and Frost, 1933) that organisms do not live in nearly pure D_2O.

Washburn and Smith (1934a) found no difference in density between purified water from the open ocean, the Dead Sea, and Great Salt Lake; the increase over normal water was approximately 2γ in each case.

Kassatkina and Florensky (1941) have determined over-all increase in density for waters of some seas and salt lakes and have separated the effects of H^2 and O^{18} (Table 6).

TABLE 6.—DENSITY DIFFERENCES OF WATER FROM SEAS AND SALT LAKES
(Kassatkina and Florensky, 1941)

Place of Sampling	Depth m	Δ%D	Δ%O^{18}	Δ d_S	Δ d_D	Δ $d_{O^{18}}$
Barents Sea, 35 miles offshore opposite Dalne in Zolentsky Bay. Aug. 20, 1938	0	−26.8	4.75	4.4γ	−5.2γ	9.6γ
Sea of Japan, near Island "Russky"	0	4.8	0.7	2.4	0.9	1.5
Black Sea, Sebastopol Bay. Nov. 15, 1937	0	5.2	1.4	3.3	1.0	2.3
Black Sea, 43°10′N., 35°45′E. Nov. 15, 1937	1700	−13.7	3.6	3.3	−2.6	5.9
Caspian Sea, 38°52′N., 51°32′E., 1933	0	6.3	0	1.1	1.1	0
Aral Sea, 5 km. south of Cape Izendy-Aral on Kulandy Peninsula. Nov. 9, 1937	0.7	−40.0	4.8	2.3	−7.6	9.9

Accuracy of the determinations, $\pm 0.2\gamma$.

They call attention to the fact that, whereas water at a depth of 1700 m in the Black Sea has the same over-all density as the surface water, the isotopic composition is quite different. They remark that, although the density of water from the open Caspian Sea is between normal fresh and ocean water, the water of Kara-bugas Gulf is much above the normal because of strong evaporation in the gulf.

The Aral Sea is highly deficient in H^2 probably because it is in part glacier-fed.

The high density of Barents Sea water, produced by abnormal content of O^{18}, is not explained.

Friedman (In press) determined H^1/H^2 for 36 samples of surface sea water from widely scattered localities. The results are accurate to ±0.1%. For all except two samples the ratio lies between 6375 and 6500. The two exceptions are from the west coast of Greenland and are low in H^2, with values of H^1/H^2 up to 7050, no doubt because of melt water from glaciers. Friedman gives his results as percentage differences from a working standard; they have

been recalculated here to approximate H^1/H^2 ratios for ready comparison with other results.

Briscoe, in his discussion of the paper by Emeléus *et al.* (1934, p. 491), reported a density of 3.0γ above normal for water of the Dead Sea; Emeléus *et al.* (1934, p. 1214) give 2.52γ. They did not determine the effects of O^{18} and H^2 separately, but this is the only result available for Dead Sea water. Probable error in both sets of data is ±0.2γ.

Isotopic Composition and Density of Fresh-Water Lakes and Rivers

Teis (1939b) has reported on the isotopic composition (density measurements) of water from some fresh-water lakes and some rivers of the U.S.S.R. Water from the Volga, Dnieper, and Ob rivers had the same density as the standard, Moscow tap water. Three Transbaikal rivers, the Argun, Gasimur, and Shilka, gave values of −2.4, −2.7, and −2.2γ with respect to Moscow water. The precision is reported as ±0.2γ. This negative anomaly is thought to be the result of melting ice from frozen ground supplying part of the water to these rivers. Ice from bore holes in this frozen ground, however, gave negative anomalies less than those of the river waters, −0.8 and −1.3γ. (It is not stated whether the ice was melted completely for these determinations. If so, then a smaller anomaly would be expected than would be shown by partial melting, such as would take place in nature.)

Water from six lakes, Senege, Pleshcheyevo, Razval, Kara-Kul, Imandra, and Baikal, gave values of +2.2, +1.8, +1.9, +1.7, +2.1, and 0.0γ, respectively. Kara-Kul is at high altitude in a dry area and was accordingly expected to give a relatively high value because of intense evaporation; that it did not is probably explained by the fact that it is fed by melt-water from glaciers.

The sample from Baĭkal was collected at a depth of 1200 m in 1935; the result on it contrasts sharply with those obtained by Vereščagin, Gorbov, and Mendelejev (1934) and by Mendelejev (1935) on samples from the same depth.

Teis concluded that lake water averages about 2γ denser than river water and that waters of lakes and rivers fed by melting ice have lower density than others.

Vereščagin, Gorbov, and Mendelejev (1934) measured the density of water collected from the surface and from 1200 m in Lake Baikal September 4, 1933. The sample from depth showed an increase in density of 2.4 in the fourth decimal place (240γ), which cannot be explained by the (dissolved) constituents. The authors recognize the possibility of increased H^2 and O^{18} at depth but do not believe that concentrations of these isotopes can explain all of the increase in density. They suggest that "molecular structure" (complexes, $(H_2O)_2$, $(H_2O)_3$, etc. ?) of the water may be responsible for a part of the difference and that this may account for some of the peculiarities of the flora and fauna of the very deep fresh-water lakes, such as Baikal and Tanganyika, whose flora and fauna differ rather sharply from those of other (shallow) fresh-water bodies in the same regions.

Mendelejev (1935) reviews the work on the sample from 1200 m in Lake Baikal but gives the difference in density as 3 in the sixth decimal place (3γ). He does not mention a redetermination or an error in the earlier work, which makes it appear that perhaps the very high value reported earlier is a typographical error, although the increase in density is clearly stated as 2.4 in the fourth decimal place in both the Russian and French versions of the 1934 paper. Experimental error is not recorded in either paper, but Mendelejev gives densities to seven places.

Mendelejev (1935) reports much more detailed work on water from Lake Baikal, results of density measurements on samples from several different levels, both as collected and after purification and distillation (Table 7).

The progressive increase in density with depth may indicate an actual gravitative fractionation, with the heavier isotopes settling out. The reversal between 1000 and 1200 m may be related to exchange with dissolved atmospheric oxygen, which contains a higher proportion of O^{18} than does ordinary water. The difference between density of the water as collected and after distillation remains essentially constant from 600 m down, indicating that the increase

in density is isotopic and not due to more dissolved material at depth.

Mendelejev points out that O^{18} is about 9 times as abundant in ordinary water as is H^2. Therefore, he reasons, most of the increase of density at depth in Lake Baikal is probably due to higher O^{18} content. It would be interesting to have this interpretation checked by an accurate determination of the effect of H^2 and O^{18} separately.

Table 7.—Variation in Density of Water with Depth in Lake Baikal (Mendelejev, 1935)

Depth (m)	Δd after distilling	Δd as collected	Δd as collected — Δd, distilled
0	0.0γ	67γ	67γ
600	0.7	74	73
1,000	2.9	77	74
1,200	2.7	78	75
1,400	3.0	78	75
1,600	4.4	83	77
1,650	5.6	—	—

Emeléus *et al.* (1934, p. 1214) report the density of water from a Tibetan lake at 13,500 feet above sea level as 1.5 ± 0.2γ above normal water.

Friedman (In press) determined H^1/H^2 for the waters of rivers from all the major physiographic provinces of the United States. For convenience in summarizing they can be divided into four groups:

(1) Streams fed by rains from "Gulf Air" (Great Lakes—Great Plains region) are relatively high in H^2; values of H^1/H^2 range from 6650 to 6695.

(2) Streams fed by moisture from the cooler North Pacific and North Atlantic are somewhat lower in H^2; R = 6710 to 6920.

(3) Snow-fed streams of the Northwest are much lower in H^2; R = 7275 to 7525. The last value is approximately that for snow itself.

(4) Rivers in the Southwest and extreme Southeast that have been subjected to excessive evaporation are higher in H^2 than any others measured; R = 6475 to 6510.

Isotopic Composition and Density of Water from Hot and Mineral Springs; Fumaroles

Shibata, Noguchi, and Kaneko (1937) made accurate measurements of the density of waters from about 20 mineral springs, hot springs, and borings within 15 km (all but two within 10 km) of the crater of Asama Volcano, Japan. Many of the results show such small anomalies that they are on the border of experimental error,

Table 8.—Variations in Density of Water from Fumaroles at Yadake Volcano, Japan (after Oana)

Fumarole	Aug. 1938		July 1939		Aug. 1940	
	T°C	Δdγ	T°C	Δdγ	T°C	Δdγ
A1	—	—	185.5	+3.4	166.4	+1.8
A2	170	+5.4	—	+3.6	164.2	+2.5
B	—	—	209	+3.6	195.3	+1.2

but it is interesting and perhaps significant that all samples are lighter than the standard, Tokyo tap water, by 0.1 to 2.0γ, ±0.1γ.

In general the anomalies are greater for water with higher temperature, greater residue on evaporation (dissolved material), larger Ca- and Cl-contents, and lower pH.

Oana (1939; 1942a; 1942b) determined the density of water from a number of hot springs and fumaroles in Japan. In general, he found that when the temperature was lower than about 60° C the density of the water was very nearly the same as that of the ground water, rain, and river water of the region. (Δd = +0.2γ to ca. − 2.0γ with respect to Tokyo tap water.) In general, the hotter the spring or fumarole, the greater the density of its water. For example, the water of a spring at Iōyama with a temperature of 85°C showed a density of 1.9γ above the standard. Fumaroles at Yadake Volcano were studied for three consecutive summers, with the results shown in Table 8. Two other fumaroles measured in 1938 gave temperatures of 91° and 210°C and Δd of +1.4γ and 5.1γ, respectively. The summer of 1938 was quite dry in the area, the one of 1939 somewhat less dry, and 1940 more or less normal. The obvious interpretation is that in the dry summers the fumaroles contained more juvenile and less vadose water than normally. Since the density is increased at this time it is concluded that the juvenile component contains appreciably more heavy water than does the vadose component. No estimates of the

amount of juvenile water present in any of the springs or fumaroles were made, however.

Teis (1946a) determined the density of 35 (purified) mineral waters, including samples from 22 springs. He found that the least-mineralized waters showed lowest density, which does not corroborate the findings of Shibata and coworkers (1937). Teis concludes that this is due at least in part to percolation of the waters through soils and other materials, which adsorb deuterium more readily than H^1, just as they adsorb ions of some metals more readily than others. Where H_2S is present, exchange enriches H_2O in H^1; H_2S in H^2. Vadose waters studied did show lowered density after percolation through soil and other materials.

Five medicinal springs at Budapest gave the same density of water as that of the Danube River, after both were purified (reported by Lányi and Arató, 1942).

Teis (1946a) investigated four waters with different CO_2 contents:

No.	Δd_S	Δd_D	$\Delta d_{O^{18}}$
1	0.4γ	−0.9γ	+1.3γ
2	0.3	−1.5	1.8
3	0.5	−1.5	2.0
4	1.3	−0.2	1.5

Probable error, ±0.1γ

The O^{18} content is almost constant and appears to be independent of the CO_2 content.

Friedman (In press) determined H^1/H^2 for water from a fumarole and a hot spring at Parícutin as 6800 and 6900, respectively. Two geysers in Yellowstone gave values of 7550, which is very close to those for glaciers and snow of that general region. Other hot springs and fumaroles in Yellowstone give values up to 12,650. These samples of water were prepared from methane and free hydrogen from the springs and fumaroles. The values for H_2 and CH_4 were not determined separately.

Variations in Density and Isotopic Abundance in Rain, Snow, and Natural Ice; Fractionation during Freezing and Thawing

General studies of the isotopic composition of fresh rain water, snow, and natural ice of various kinds have been made; also laboratory studies of isotopic distributions during artificial freezing and thawing. Riesenfeld and Chang (1936a) attempted to demonstrate a fractionation by freezing out a fraction of a per cent of the water from a large vessel onto a rotating copper tube. When the ice thus formed was melted and the density of the resulting water determined, it was the same, within experimental error, as that of the whole water sample. They concluded that the exchange was so rapid between the ice and the rest-water that no measurable enrichment was produced.

Bruni and Strada (1934) reported concentrations up to 0.414% H_2^3O by a nine-step fractional crystallization, but later Bruni (1934a; 1934b) indicated that the original work was incorrect and that if any separation takes place it certainly is less than 1/10,000 and probably less than 1/100,000 when the original mass is reduced to 1/14,000.

Gilfillan (1934b) discussed the correction by Bruni and showed theoretically that a one-step partial freezing of water should increase the density of the frozen fraction by 0.22γ. He took samples of water and, during stirring, froze half the amount taken, and repeated the operation 8 to 12 times:

Crystallizations	10	10	8	12	8	12
Δd (γ)	1.2	1.0	0.9	1.1	0.7	1.3

Average deviation of duplicate determinations was 0.1γ. The average effect per crystallization was 0.1γ, in fair agreement with the calculations. (Studies by other workers indicate that, if Gilfillan had frozen less than half, say 10% of each sample, the change in density would have approached the theoretical more closely.) This change in density is due primarily to H^2, but there is also a slight change in the isotopic composition of oxygen during fractional crystallization. The freezing point of D_2O is given as 3.82°C; of $H^1H^1O^{18}$ as −0.1°C.

Emeléus *et al.* (1934, p. 1216) reported that the ice first formed in a refrigeration plant showed an increase of density of 1.05γ with respect to the original water. The residual water gave a value of −2.73γ, and hoar frost (on the pipes?) −2.94γ. Probable error was ±0.2γ.

Teis and Florensky (1941) studied the separate effects of changing concentrations of H^2 and O^{18} during the freezing of water. They found that O^{18} accumulates, and H^2 is impoverished in the first-formed ice with respect to

the initial water. The greatest differences, up to -8.0γ for H^2 and $+14.0\gamma$ for O^{18}, were observed as freezing began, and they levelled off as the amount of solid phase increased. When approximately one-third of the water had crystallized, the differences were about -2.0γ and $+2.0\gamma$, respectively, for H^2 and O^{18}. Probable error was $\pm 0.2\gamma$.

Variable conditions influence the amount, but not the direction, of fractionation. Stirring of the water during freezing caused less fractionation, as did lowering the temperature of freezing. For example, in a run that was not stirred $\Delta d_{H^2} = -8.0\gamma$ and $\Delta d_{O^{18}} = +14.3\gamma$; in an analogous run that was stirred $\Delta d_{H^2} = -0.7\gamma$ and $\Delta d_{O^{18}} = +7.1\gamma$. Freezing at 0°C produced values of -8.0γ and $+14.3\gamma$; an analogous run at -2.1°C, values of -5.9γ and $+9.0\gamma$.

Friedman and Epstein (unpublished results; personal communication from Friedman) found that when 20% of the water in a flask was frozen during vigorous shaking the ice was enriched in both H^2 (5.92%) and O^{18} (0.65%), which does not agree with the findings of Teis and Florensky that the first-formed ice is enriched in O^{18} but depleted in H^2.

For a study of natural fractionation, Teis and Florensky collected, from snow pools and spring rivulets, ice as it began to form after sundown. The samples gave values of -4.2 to -9.3γ for Δd_{H^2} and of $+2.4$ to $+12.6\gamma$ for $\Delta d_{O^{18}}$. One sample with very large ice crystals gave a negative value (-5.7γ) for $\Delta d_{O^{18}}$. They conclude that detailed laboratory studies of freezing and thawing can help in the study and interpretation of the variation of isotopes in natural ice and the water from which it crystallizes and into which it melts.

Several studies have been made of fractional thawing and freezing in nature with resultant changes in isotopic composition and density—melting of glaciers, thawing and freezing of snow banks, isotopic composition of freshly fallen snow, etc. For example, Eucken and Schafer (1935) found that the enrichment of H^2 in glacier ice is greater as the amount of remaining ice decreases. In narrow tongues of deep valley glaciers the enrichment may be 50 per cent greater than the H^2 content of normal water. They also reported that the heavy isotopes concentrate in the ice during partial freezing and the light isotopes go into the water preferentially as melting begins. This agrees with Friedman's results. They give a calculated diagram of the system D_2O—HDO—H_2O. The melting point of HDO, found by extrapolation, is given as 2.50°C.

Teis and Florensky (1945) studied the isotopic composition of glaciers and their meltwater. They measured seven samples of glacier ice, meltwater, and Ingur River water, collected in July and August 1939 (Table 9).

One sample of glacier ice contained more deuterium than normal river water; all other samples studied were lower in deuterium than ordinary river water. The O^{18} content of all the samples equalled or exceeded the O^{18} content of normal river water. Three samples of Ingur River water were collected at equal intervals. The upper one, from near the glacier, has an isotopic composition similar to glacial meltwater, whereas the lower two are almost identical to normal river water because of dilution by ordinary surface water.

Teis (1946b) reported a more elaborate set of experiments and the results of studying another group of snow and ice samples (Table 10).

To aid interpretation of the results some laboratory experiments were undertaken. Ice with a volume of 117.5 cc was melted at 17.5°C in four fractions (I to IV) over a period of 3.5 hours. The ice contained 0.1364% H^2. The density changes recorded are in γ with respect to the water of the entire sample (Table 11).

The first fractions melted in both cases contained considerably less deuterium than the original sample; in the other fractions the deuterium increases more rapidly than is indicated by calculations. The density increases more rapidly when water is removed from contact with the ice as it melts.

Density (and content of H^2) depends upon the stage of melting, contact of ice and meltwater, temperature of melting, and possibly on time of melting and other factors not considered in this study.

Teis and Florensky (1940) made a detailed study of the water obtained by melting freshly fallen snows, and reported the separate effects of H^2 and O^{18} variations. They confirmed the over-all figure of about -2.0γ for freshly fallen snow, previously reported by Riesenfeld and Chang (1936b) and by Harada and Tita

TABLE 9.—EFFECTS OF H^2 AND O^{18} ON THE DENSITY OF WATER FROM GLACIERS AND THEIR MELT-WATER (Teis and Florensky, 1945)

No.	Location and description of samples	Δ d		
		Δd_S	Δd_D	$\Delta d_{O^{18}}$
1	Melt-water from surface of Adishi Glacier	5.8γ	−5.8γ	11.6γ
2	Ice from Adishi Glacier	3.6	3.5	0
3	Ice from Yukhvan Glacier	−0.5	−3.9	3.4
4	Water from Gul Glacier	1.6	−3.0	4.6
5	Water from Ingur River, near village of Ushgul	3.4	−6.2	9.6
6	Water from Ingur River, near village of Latali	−1.2	−1.3	0
7	Water from Ingur River, near village of Khaishi	−1.2	−1.3	0

Probable error was ±0.2γ.

TABLE 10.—EFFECTS OF H^2 AND O^{18} ON THE DENSITY OF SNOW AND ICE (Teis, 1946b)

No.	Specimen; conditions	Δd_S	Δd_{H^2}	$\Delta d_{O^{18}}$
1	Coarse firn; last stages of melting in sun	4.7γ	3.7γ	1.0γ
2	Firn ice that has been consolidated by pressure; final stages of thawing; clear layer.	7.7	1.4	6.3
3	Layer of firn, 3 to 5 mm. Like No. 4, but has melted slowly.	−2.4	−6.1	3.7
4	Snow crust in woods; partly melted; collected in thawing condition.	0	0	0
5	Granular remains of melting drift.	−2.2	−6.4	4.2
6	Small pool beside No. 5.	−6.1	2.0	−8.1
7	Compact firn from under last remains of snowdrift in shady spot; thawing.	2.1	0.3	−1.8

Probable error in density determinations, ±0.2γ.

TABLE 11.—CHANGES OF WATER DENSITY DURING MELTING OF ICE (Teis, 1946b)

Fraction	Volume of Fraction	V (remain.) / V (orig.)	Change of concentration of D with respect to initial sample					
			Solid (Calc.)		Solid (Found)		Melted ice	
			%	γ	%	γ	%	γ
I*	27	—	—	—	—	—	−0.0287	−25.7
II	64	0.77	0.0008	0.7	0.0098	8.7	0.0082	7.3
III	15	0.22	0.0024	2.1	0.0109	9.7	0.0099	8.8
IV	11.5	0.099	0.0076	6.8	0.0208	18.5	—	—
A*	30	—	—	—	—	—	−0.0217	−19.2
B	60	0.776	0.0005	0.4	0.0020	1.8	0.0018	1.6
C	28	0.331	0.0031	2.7	0.0115	10.2	0.0105	9.3
D	16.5	0.123	0.0058	5.4	0.0135	12.6	—	—

* For I to IV the ice was suspended above a funnel, so the conditions of melting were analogous to those of an icicle, or a wasting glacier, where the water is removed from the remaining ice continuously. For A to D the ice remained in a vessel in contact with the meltwater, as in stagnant glaciers, or melting river ice. The ice contained 0.1130% H^2. T = 17.5°C; 134.5 cc of ice were melted in 3.25 hours.

(1935), but determined that the effect of H^2 is -6.0 to -8.5γ and that of O^{18} is about $+4.0$ to $+6.5\gamma$, with an accuracy of $\pm 0.2\gamma$. In other words, they found that there is a deficiency of heavy hydrogen and an excess of heavy oxygen in snow as it forms. They also studied snow banks that had partly thawed and wasted away and found that H^2 and O^{16} had accumulated with respect to freshly fallen snow. For two occurrences Δd for H^2 was $+2.5$ and $+3.1\gamma$; for O^{18}, $+0.8$ and -2.1γ.

Harada and Titani (1935) collected samples throughout a rain and obtained the following results:

(1) A 340-cc sample collected at the beginning of the rain gave $\Delta d = +1.6\gamma$ with respect to ordinary (tap) water.

(2) A sample of 1,180 cc collected during the middle period of the rain gave $\Delta d = -1.3\gamma$ and

(3) The final 30 cc gave $\Delta d = -1.9\gamma$.

Riesenfeld and Chang (1936b) remark that the results of Harada and Titani indicate that rainwater is 0.7γ lighter than ordinary surface water. They point out, however, that this is based on the results of the study of a single rain and that a great many more studies should be made before this result is accepted as valid, although theoretical calculations indicate that a difference of approximately 1.0γ is to be expected.

Teis (1939a) confirmed the results of Harada and Titani (1935) that the first part of a rain is relatively heavy, but did not get progressively lighter samples to the end of the rain as they did:

No.	*Time*	*cc*	$\Delta d(\gamma)$
1	12h–13:15	75	+0.4
2	13:15–14:30	150	−2.3
3	14:30–15:45	75	−2.3
4	15:45–18:15	60	−2.3
5	18:15–19:15	40	−0.3

Probable error, $\pm 0.2\gamma$.

Water collected during two May thunderstorms in Moscow and one in September on the coast of the Black Sea gave values of $+2.7$, $+2.7$, and $+2.1\gamma$, respectively. Two samples of rain plus hail and one of rain alone collected during a single thunderstorm gave values of $+0.5$, $+0.1$, and $+2.7\gamma$. Rain collected from the same storm after the hail had ceased gave a value of -0.9γ. Melted hail alone showed -1.5γ. Average for all samples of one long rain was -1.6γ.

The positive values obtained for rain collected during thunderstorms may be explained by exchange between atmospheric oxygen and the water vapor of the clouds brought about by the electrical phenomena of the storm.

Density of Atmospheric Moisture Condensed Artificially

Okabe and Titani (1937) condensed 50 to 135 cc samples out of the atmosphere artificially and measured their densities, for a comparison with results on natural precipitation. They chose all kinds of weather for their experiments, ranging from clear with relative humidity = 47% to rainy with relative humidity = 88%. All of the samples showed $\Delta d = -0.8$ to -6.8γ with respect to Osaka tap water. The average of 22 determinations was -3.7γ, but there was no apparent relation to relative humidity or other factors. Accuracy of measurements was $\pm 0.5\gamma$.

The isotope ratio of water in the atmosphere depends upon at least the temperature and rate of evaporation and source of the water evaporated. The isotopic content of condensates depends upon the temperature and rate of condensation, as well as on the ratio existing in the atmosphere at the time of condensation, so it is not surprising that considerable variation has been noted. Atmospheric moisture appears to be consistent, however, in being always of lower density than normal water, which explains in part why snow that crystallizes therefrom is lighter also.

Atmospheric Hydrogen

Harteck and Suess (1949) state that the atmosphere contains about $5 \times 10^{-7}\%$ of free hydrogen. They found that this hydrogen to contain $12 \pm 7\%$ more deuterium than normal hydrogen (of water), whereas if it were in equilibrium with the water vapor of the atmosphere it would be expected to contain less deteurium than normal hydrogen by a factor of four.

Isotopic Composition of Hydrogen in Organic Compounds

Dole (1934c), using electrolytic oxygen prepared from his standard water, obtained the

same density for water prepared from the hydrogen of benzene and for the standard water. He concluded that there is no significant natural segregation of the isotopes of hydrogen in organic substances, although earlier (1934a; 1934b), using tank oxygen, he had apparently found enrichment of H^2 in benzene, kerosene, and honey. From the findings of Lewis (1933) and of Taylor, Swingle, Eyring, and Frost (1933) that organisms do not live in nearly pure D_2O, he had expected to find the hydrogen of organic substances impoverished in H^2. In a longer paper, Dole (1936d) discussed possible sources of error in hydrogen-isotope determination by the density method and concluded that failure to determine the isotopic composition of the oxygen used in combustion is probably the only significant one.

Filippova (1935a) found that petroleum products ("motor petroleum" from Machach-Kala) contain more H^2 than does normal (surface) water. His value is 50% more H^2 in the hydrogen of petroleum than in that of normal water. When drops of the petroleum were allowed to fall on a red-hot surface and combustion products were partly condensed, the proportion of H^2 was still higher, indicating a *preferential condensation* of D_2O.

In a later note (Filippova, 1935b) he repeated the results recorded above, but pointed out that, if the tank oxygen used in obtaining them was abnormally heavy, then the recorded ratio of deuterium is too high, but he did not report an investigation of the O^{18} content of the tank oxygen, nor did he estimate how much too high the value of 1.5 parts H^2 to 5,000 parts of H^1 is. If corrections of the order of those made by Dole (1934c) for this error are applied, then the excess H^2 would be only 10 to 30%.

Bertram and Mendel (1936) suggested that in petroleum from which most of the lighter fractions had escaped (asphalt) an abnormal concentration of H^2 might be expected. They obtained water by burning asphalt and found it to be 11γ heavier than normal water. Even allowing for excess O^{18} in atmospheric or tank oxygen the water thus obtained would be 6 – 8γ heavier than normal water.

Snow and Johnston (1934) found that hydrogen in butane is enriched some 30 per cent in H^2 over that in ordinary water. The effect of excess O^{18} in the oxygen used for combustion was calculated in giving this result.

Maillard (1936; 1937) obtained values of H^1/H^2 of 1920 and 2500 for water prepared from the hydrogen of natural gas from Pechelbronn and Peron, respectively. The determination was made by comparing index of refraction and freezing point of water produced by combustion with those of ordinary water. Error in index determination is estimated to be not more than 4%; in temperature, 0.3%. He took the value for ordinary water to be 4000, so his results indicate increases of about 100 and 60 per cent respectively; with electrolytic oxygen these values would reduce to about 70 and 30 per cent.

Greene and Voskuyl (1934) obtained values from natural gas and corn oil that would just about cancel out with the correction applied for electrolytic oxygen.

Washburn and Smith (1934b) and Smith (1934b) report that water from sap of a willow tree and water formed by combining hydrogen from the wood of the tree with standard oxygen both show a density about 3 γ above that of standard water.

Density of Water Associated with Petroleum

Scott (1934) measured the density of water from two oil wells. The wells, one producing from the Oligocene and the other from the upper Eocene, were more than 5,000 feet deep (locations not given). The water was separated from oil and other impurities; in both cases the density was the same as that of ordinary water within the limits of measurement, 2.0 γ.

With somewhat greater precision ($\pm 0.2\gamma$) Emeléus *et al.* (1934, p. 1948–1949) measured the density of water from the "Asmari limestone," of lower Miocene age, in the Persian oil fields and obtained a value of 1.9 γ above that of normal water. They suggest that evaporation of part of the water at the time of deposition of the strata may have produced abnormal density.

The samples studied by Scott could have had equally high densities and no abnormality detected by the methods used. Combustion was not involved in either determination, of course, so the only uncertainty is the limit of error in the density measurements.

Helium

He^3 was originally observed (Oliphant, Harteck, and Rutherford, 1934; Oliphant, 1936) as

a product of nuclear reactions, and it was supposed that naturally occurring helium consisted entirely of He^4. In 1939, however, Alvarez and Cornog (1939a) demonstrated the presence of He^3 in ordinary (gas-well?) helium. Later (1939b) they estimated the relative abundance of the two isotopes for both atmospheric and gas-well helium. They found about 12 times as much He^3 in atmospheric as in gas-well helium, He^4/He^3 for the former was given as 10^7 and in the latter as 10^8. Libby (1946) offered an explanation for the greater concentration of He^3 in the atmosphere: That it is the decay product of H^3 that is produced in the upper atmosphere by cosmic-ray bombardment, along with C^{14}.

Aldrich and Nier (1946) repeated the work on the abundance of He^3 in atmospheric and well-gas helium. Their relative values check those of Alvarez and Cornog very closely (He^3 about 12 times as abundant in the atmospheric He as in well-gas He), but the absolute values show He^3 to be about 10 times as abundant as was indicated by the earlier workers. Aldrich and Nier obtained for atmospheric He (from Air Reduction Sales Co.) $He^4/He^3 = 9 \times 10^5$ and for well-gas helium, 7×10^6. These values were later changed (Fairbank, Lane, Aldrich, and Nier, 1947) by applying a correction for the difference in pumping speeds of He^3 and He^4 in the mass spectrometer pump, and led to 7.7×10^5 and 6.25×10^6, respectively.

Bainbridge and Nier (1950) report these results without indicating an adopted, or preferred, value.

Aldrich and Nier (1948) have studied the relative abundance of the isotopes of helium in a number of natural materials. For their standard they took atmospheric helium ($He^4/He^3 = 8.3 \times 10^5$).[4] They were unable to detect He^3 in any of five samples of radioactive minerals studied, which indicates that all the helium in these materials is formed from α-particles produced by radioactive decay.

He^4/He^3 for seven beryl samples from Finland, Sweden, and the United States varied from 8.3×10^5 to 2.0×10^7. The absolute amount of He^3 per gram of mineral did not vary systematically with this ratio or with the age of the mineral. Neither could the amount of radiogenic A^{40} be correlated with any factor.

Two samples of spodumene showed much higher He^3 content than any other materials studied; $He^4/He^3 = 8.3 \times 10^4$ and 4.1×10^4. Aldrich and Nier suggest that the reaction originally proposed by Hill (1941),

$$Li^6(n, \alpha)H^3 \xrightarrow{-\beta} He^3$$

to explain the He^3 in natural gas may have been effective here. The source of neutrons proposed by Hill is cosmic radiation. The setting of the two samples of spodumene suggests another possible explanation. The sample taken at the earth's surface has a He^3/He^4 ratio only about a fifth as large as the sample collected between 20 and 30 feet below the surface.

From these considerations it is evident that the chances of sound interpretation would have been enhanced materially had it been possible to study thoroughly the pegmatites from which the beryl and spodumene came. Since that was not possible, it would be well to have similar determinations made on material whose relationships to associated minerals can be ascertained before it is collected. The apparent anomalies could possibly be explained by the presence and distribution of radioactive minerals. For example, if the spodumene sample that showed a high He^3 content was closely associated with uranium and beryllium minerals, then the Li^6 (n, α) H^3 reaction may have been brought by neutrons produced by bombardment of the beryllium by α-particles from the uranium series of elements. Since the neutron flux produced by cosmic radiation in rocks, and its variation with depth, are not known it might be necessary to carry the study to depths much greater than the 20–30 feet mentioned above in order to demonstrate whether the sound of the neutrons is cosmic ray bombardment or whether some or all of the effective neutrons are produced by rays from radioactive elements in the rocks.

Coon (1949) repeated the determinations of the He^4/He^3 ratio in atmospheric and gas-well helium using a technique different from that of Aldrich and Nier, but which checked their results very closely.

[4] In the original paper this value is given as $He^3/He^4 = 12.0 \times 10^{-7}$, and the other values are reported as He^3/He^4. They have been recalculated to He^4/He^3 to facilitate comparison with the earlier work reported above.

Lithium

Brewer and Baudisch (1937) studied the isotopic composition of lithium in the mineral springs at Saratoga, N. Y., and in the Upper Cambrian Cryptozoon reefs of the area. They obtained $Li^7/Li^6 = 11.8 \pm 0.1$ for both materials. Previous work (sources not specified) had given values of 11.6 to 11.8, so they conclude that the ratios found at Saratoga do not differ appreciably from normal. Bainbridge and Nier (1950) accept a value of 12.29 ± 0.2 for Li^7/Li^6.

T. I. Taylor (1939) has performed an experiment in the fractionation of lithium isotopes that is of geologic interest. He studied the reaction

$$Li^+ + \text{Na zeolite} \rightleftarrows \text{Li zeolite} + Na^+$$

by running solutions of lithium salts through a 100-foot column packed with a sodium zeolite. He found that "appreciable" changes in the isotope ratio for lithium were produced, but no quantitative results are recorded. He concludes that the properties of isotopes of the lighter elements are different enough so that chemical separation can be effected, but not different enough to interfere with the use of isotopes as tracers and in exchange reactions. (*See* discussion of work of Taylor and Urey in the section on Potassium for semiquantitative work of this nature on lithium.)

Boron

Thode, Macnamara, Lossing, and Collins (1948) have determined variations in the isotopic composition of boron minerals from various localities (Table 12). The determinations were made with a mass spectrometer.

The variation among the samples is about 3.5%, whereas the relative precision of the method used is ±0.1%. The absolute accuracy is ±0.5% or better. It is apparent, therefore, that the differences found are real and significant. No explanation of the differences is attempted, but Thode and his coworkers plan laboratory experiments on isotopic fractionation of boron in steam distillation of boric acid. They also plan to determine the isotopic composition of boron from primary minerals such as tourmaline and to make detailed studies of variation with depth and other factors in a given deposit, such as the basins of southern California. When these studies have been completed, it should be possible to suggest interpretations of the results.

Table 12.—Isotopic Composition of Boron from Various Sources (Thode, et al. 1948)

No.	Mineral and Locality	B^{11}/B^{10}*
1	Sultantchair, Turkey	4.291
2	Kernite (Rasorite), Boron, California	4.322
3	Borax, brine of Searles Lake, California	4.370
4	Boric acid, source unknown	4.369
5	Stassfurtite, Stassfurt, Germany	4.422
6	Ulexite, Tres Moros, Argentina	4.270
7	Tincal, hot springs of Tibet	4.326
8	Boric acid vapors, Tuscany, Italy	(a) 4.416 (b) 4.411
9	Pandermite, Sultantchair, Turkey	4.297

* Bainbridge and Nier (1950) recognize, on the basis of this work by Thode and his coworkers, the variability in the value of B^{11}/B^{10}, so their adopted value is 4.27 − 4.42.

Carbon

Estimates of Relative Abundance of C^{12} and C^{13}

There are two stable isotopes of carbon, C^{12} and C^{13}. The relatively large difference in the masses of these two atoms, the ease with which CO_2 is handled in the mass spectrometer, and the wide distribution of carbon in nature make this element a logical one to study for isotopic fractionation and interpretations. Numerous workers, therefore, have concerned themselves with the distribution of the stable isotopes of carbon in nature.

Nier and Gulbransen (1939) published the first of these studies. They measured variations up to 5% in the C^{12}/C^{13} ratio. These variations are significant since the limit of error was about 0.5%. They obtained the values shown in Table 13.

Their results indicated that C^{12} tends to concentrate in vegetable material; C^{13}, in carbonates.

Murphy and Nier (1941) continued these

TABLE 13.—ISOTOPIC COMPOSITION OF CARBON FROM VARIOUS SOURCES (Nier and Gulbransen, 1939)

Material; locality	C^{12}/C^{13}*
Limestone, Grenville, New York	87.9
Na_2CO_3, derived from Michigan limestone	88.3
Limestone, Vermont (Ordovician)	88.5
Clam shell, Boston	88.6
Clam flesh, Boston	90.1
Diamond, Africa	89.0
Meteorite	89.4
Graphite, Ceylon	89.8
Air, collected 3/22/28, Boston	89.9
Air, collected 3/14/28, Boston	92.5
Oil, West Texas	91.2
Dry ice prepared from coal	91.2
Coal	91.8
Wood	91.5

* Bainbridge and Nier (1950) adopt a value of 89.3 for this ratio.

TABLE 14.—ISOTOPIC COMPOSITION OF CARBON FROM VARIOUS SOURCES (Murphy and Nier, 1941)

Material	No. Samples	C^{12}/C^{13}
Limestone	10	89.2
Coal	10	91.8
Wood	7	91.8
Petroleum	6	92.5
Bituminous shales	7	92.5
Torbanite and oil shales	3	91.7
Meteoritic carbon	7	91.3
Graphite	1	90.2
Zeolitic calcite	1	89.9
CO_2 in air, Minneapolis	1	91.5
Lycopodium spores	1	93.1
"Bolkashite", algae	1	92.8
Marine shell	1	89.5
Sea water	1	89.3

Limit of error was about 0.5%.

measurements and extended the results (Table 14).

These results confirmed the concentration of the heavier isotope in carbonates and the lighter one in wood and coal, but petroleum and bituminous shales showed even greater concentration of C^{12}. No age effect was noted in limestone, coal, or wood. Limestone from Precambrian to Recent was studied; coal from Pennsylvanian to Pliocene; wood from Pleistocene to Recent. Limestone, marine shells, and CO_2 from sea water all show essentially the same ratio. The systematic differences (about +.9%) between these results and those of Nier and Gulbranson may be due to use of different mass spectrometers.

Baertschi (1952) reported the results of experiments that may help to explain the enrichment of C^{12} in plants. He found that $BaCO_3$ formed by absorption of CO_2 in a solution of $Ba(OH)_2$ is enriched in C^{12} by a factor of $1.013 \pm .003$. He explains the fractionation as a function of the kinetic behavior of the $C^{12}O_2$ and $C^{13}O_2$ molecules and suggests that plants may take up C^{12} preferentially by the same mechanism.

Wickman (1941) made an interesting interpretation from the C^{12}/C^{13} ratios in calculating the total amount of coal and bitumen. He assumed that the value for diamond (89.5) represents the original isotopic composition of terrestrial carbon. CO_2 in the hydrosphere (0.02) and in the atmosphere (0.0004) were disregarded. Carbon of the biosphere was added to that of coal and bitumen, and a value of C^{12}/C^{13} for this combination of 92.1 was taken. For limestone and dolomite C^{12}/C^{13} was taken as 89.2. Then

$$\frac{89.2A}{A+B} + \frac{92.1B}{A+B} = 89.5$$

where A = limestone + dolomite, and B = coal + bitumen.

$$A/B = 8.65$$

Assuming Goldschmidt's figure for total CO_2 in carbonate to be correct ($A = 6.56$ kg CO_2/cm²) then the total amount of coal and bitumen, $B = 0.76$ kg CO_2/cm².

West (1945, p. 414) determined that $C^{12}/C^{13} = 94.1 \pm 0.4$ for oil and gas from 32 wells in two fields in Kansas and one each in Texas and Wyoming. Petroleum from one well in Oklahoma and three samples of hydrocarbons from well cuttings gave 93.2, 93.2, 91.6, and 93.4, respectively. The lighter isotope had no doubt escaped preferentially from the hydrocarbons, and the same may have been true of the petroleum from the Oklahoma well.

West also determined the C^{12}/C^{13} ratio for three weed samples and obtained values of 92.5, 92.6, and 92.7.

Rankama (1948a, p. 204–206) tabulated and plotted these results of Nier and Gulbransen, Murphy and Nier, and West and added one new determination of his own for graphite and seven for bituminous sediments. The new values fell in the same general ranges as the older ones. He noted that the carbons of meteoritic origin show values of C^{12}/C^{13} (89.8 to 92.0) intermediate between those of inorganic carbon (87.9 to 90.2) and organic carbon (90.3 to 93.1). He assumed, therefore, that meteoritic carbon gives an approximation of the primordial isotopic composition of the carbon of the solar system.

In another paper Rankama (1948b, p. 410–413) summarized the results on carbon again and added 11 new results on carbon from *Corycium* (a supposed Precambrian fossil) and from slate and on graphite from several phyllites and schists. Graphite from Parainen gave a value for C^{12}/C^{13} of 88.4; the other samples ranged from 90.2 to 92.9. Rankama concluded that all the material, except the Parainen graphite, was of organic origin and that *Corycium* is a definite fossil of Precambrian age, the oldest ever identified with certainty. Rankama says that the results of his measurements are accurate to 0.5%.

Hutchinson (1949) objected to these interpretations of Rankama's on the basis of a statistical treatment of the data given in Rankama's own papers, and because the estimated amounts of oxidized carbon ($CaCO_3$) and reduced carbon in the earth's crust, with the isotopic compositions given by Rankama, would not yield an original carbon with the isotopic ratio of the carbon in meteorites. Hutchinson agrees that *Corycium* is probably of organic origin not because its isotopic composition is significantly different from inorganic carbon of sedimentary rocks (limestone), as Rankama stated, but because it is similar to that of bituminous and carbonaceous sediments and significantly different from igneous carbon. Rankama (1950) answered these arguments in a discussion and maintained his original point of view.

Both Hutchinson and Rankama emphasize the need for more analyses of meteoritic and igneous carbon. Trofimov (1950) analyzed the carbon from 39 meteorites—26 stony and 13 nickel-iron. The total range in C^{12}/C^{13} was 89.6 to 91.8—almost exactly the range of the seven samples listed by Rankama. The stones averaged 90.61; the irons 90.68, an insignificant difference. The average value for meteorites given by Rankama is 91.26.

It is by no means certain that meteoritic carbon, or igneous carbon, or the carbon of diamonds has the isotopic composition of the original carbon of the earth. Neither is it certain that meteoritic carbon, or the average terrestrial carbon, is representative of the rest of the carbon in the solar system.

It does appear certain, however, that none of these types of carbon, or the average, can represent the cosmic abundance of carbon isotopes. C^{12}/C^{13} ratios have been measured for certain kinds of stars, and they differ greatly from the values for terrestrial carbon and vary markedly among themselves. For example, Menzel (1930) determined that C^{12} is no more than 10 times as abundant as C^{13} in some N-type stars. Sanford (1932) found that the spectra of R- and N-type stars give convincing evidence of C^{13}/C^{12} ratios much greater than that of terrestrial carbon. Shajn (1942) determined C^{13} in various N-type stars to range from 0.05 to 0.5 (C^{12}/C^{13} = 19 to 1). McKellar (1947) reported that R-type stars appear to be divided into two groups insofar as carbon isotopes are concerned: (1) C^{12}/C^{13} = 50 (same order of magnitude as meteoritic and terrestrial carbon), and (2) C^{12}/C^{13} = 3.4. Greenstein, Richardson, and Schwarzschild (1950) estimate that $C^{12}:C^{13}$ for the sun's atmosphere is greater than 36:1. The estimate for the sun's interior, derived from estimates of the nuclear cross sections, is 5:1.

Bethe (1939, p. 446) interprets these differences in terms of stellar evolution. He points out that C^{12} and C^{13} act as catalysts in the nuclear reactions that produce helium from hydrogen. The ratio C^{12}/C^{13}, therefore, does not become constant until stellar evolution has reached a stage where these nuclear reactions are no longer operative.

Bobrovnikoff (1930) and Swings (1943) have established the presence and variability of C^{13} in comets.

Many more determinations of C^{12}/C^{13} ratios

in rocks and minerals have been made recently. For the most part they confirm previous results. Such new interpretations as have been suggested are tentative and uncertain for the same reason as the earlier ones were—the very considerable overlap in the values of C^{12}/C^{13} for carbon from various sources.

Mars (1951, p. 133), for example, reports this ratio for 18 Swedish samples of anthracite, graphite, pitch, bitumen, and bituminous coal and obtained values ranging from 88.4 to 92.5, with an error of not over ±1.0‰. For 23 samples of limestone, spilite, uralite porphyry, lime-bearing quartz porphyry, calcite veins, and calcite dikes from Sweden, he obtained values of 88.1 to 89.8 (one value of 90.1 is questioned). He states that these measurements confirm the results obtained by earlier workers. Alghough no over-all interpretation is suggested, Mars does make some interesting observations on the results: (1) Graphite and carbonate carbon in the same mineral association have similar ratios, (2) there is lack of similarity among different types of carbon in the same association, and (3) anomalous abundance ratios (appear to be) characteristic of certain geological formations.

Wickman, Blix, and Von Ubisch (1951, p. 144–148) determined C^{12}/C^{13} for 45 samples of 11 carbonate minerals other than $CaCO_3$ and compared their results with those of earlier workers on 19 samples of calcite and limestone. Six of the ratios, two each for cerussite, magnesite, and siderite, are slightly above the highest value given for calcite and limestone; all the other values for these minerals and all those obtained for azurite, dolomite, malachite, phosgenite, rhodochrosite, smithsonite, strontianite, and witherite fall within the calcite range (87.8–89.9). They regard the results as accurate to within 0.3 unit. Most of them, except the ones for which only one or two values are given, cover the range. Dolomite forms a notable exception; all its values are below 89. The authors tabulated the occurrences of the samples and observed that the carbonates from the zone of oxidation of ore bodies all showed values above 89. From this they concluded that the dolomites were enriched in C^{13} during the change from calcite to dolomite by percolating $MgCl_2$ solutions. No explanation of the concentration of the lighter isotope in oxidation zones is attempted; the authors hope that "further investigations will give us a clearer understanding of the variation of the distribution of the C^{12}/C^{13} values of the ore-vein minerals and the oxidation-zone minerals".

Von Eckerman, Von Ubisch, and Wickman (1952) reported C^{12}/C^{13} ratios for 23 carbonate-rich intrusive rocks (carbonatites) from Älno, Sweden, and Fen, Stjernö, and Seiland, Norway. The values ranged from 88.5 to 89.4. For the Älno samples the accuracy is recorded as within 0.3 unit and for the other samples within 0.1 unit. Rocks consisting mostly of dolomite have a lower ratio (88.5 to 88.7) than those from the same area composed largely of calcite. The calcite-rich rocks from all the areas studied showed about the same ratio (88.9 to 89.4). Iron-rich dolomitic rocks (rauhaugite, $Dol_{70}Ank_{30}$) gave a lower ratio (88.83) than iron-poor ones ($Dol_{90}Ank_{10}$), which gave a value of 89.16. The authors conclude that these results confirm the deduction (Wickman, Blix, and Von Ubisch, 1951) that cation metasomatism gives enrichment of C^{13}. The dolomite-rich rocks are thought to have originated by metasomatic replacement of calcium by magnesium; iron may subsequently have replaced a part of the magnesium.

Wickman and Von Ubisch (1951) describe from the island of Gotland Silurian limestone reefs with vugs containing two generations of calcite crystals. They determined the C^{12}/C^{13} ratio, with an accuracy of 0.1 unit, for each occurrence separately:

Material	C^{12}/C^{13}
Matrix	88.18
Older calcite crystals (with yellow coating)	88.36
Younger calcite	88.48

Two explanations of the differences are suggested: (1) Oxidation of original organic matter in the reef is responsible for the results, and (2) calcium carbonate has been slowly extracted from the reef in a kind of autometasomatism, which would leave the matrix impoverished in C^{12} and the new crystals thereby enriched in C^{12}. They conclude that there was not enough organic matter in the reef to explain the observed differences and that the second explanation is more plausible. The calculated separa-

tion factor (88.48/88.18 = 1.003) is a reasonable one under the second hypothesis, but does not prove it to be the correct one.

In the same paper, Wickman and Von Ubisch (1951) compare the isotopic compositions of carbon samples from graphite and limestone or calcite from the same deposits (Table 15).

Rankama (1948b, p. 410) obtained a value of 88.4 for the same kind of graphite from Parainen, but the difference may be due largely or entirely to instrumental differences.

Graphite in limestone may be formed (1) from organic matter, (2) by reaction between limestone and an invading magma, (3) by reduction of magmatic gases such as CO_2 and CO, or (4) by combinations of (1), (2), and (3). C^{12}/C^{13} is commonly greater than 91.0 for organic matter and less than 90.0 for limestone, but (3) and (4) would give intermediate values that cannot be evaluated accurately at present.

Wickman and Von Ubisch conclude that the graphite has not been derived from the limestone, but that their data do not make it clear whether it is to be regarded as hydrothermal in origin or a mixture of reduced organic and inorganic carbon. They remark that more examples, especially from younger deposits, should be studied.

Wickman (1952) has reported on the relative abundance of the carbon isotopes in 105 plants representing all the major systematic groups. Values of C^{12}/C^{13} ranged from 89.19 to 91.43 and averaged 90.57. The accuracy was 0.1 unit. This is at variance with the results given by Rankama (1948a, p. 205) for seven plants, which ranged from 91.5 to 93.1 and averaged 91.9. A part of this difference is almost certainly due to differences in the instruments used, because Wickman's highest ratio is about the same as the lowest given by Rankama. A part of the difference, however, may be due to the fact that almost all the plants used by Rankama are land plants from humid regions, which characteristically have high ratios.

Wickman found no systematic differences between the groups of plants, or between similar plants grown at different latitudes. Differences did show up, however, between plants grown in different biotopes, and appear to be related to the varying intensity of the local carbon-dioxide cycle. Aquatic plants, in general, have lower C^{12}/C^{13} ratios than terrestrial ones, and marine plants are lower (av. 89.71) than lacustrine ones (av. 90.42). Among terrestrial plants, those growing in deserts show the lowest ratios (about the same as marine plants), tropical rain-forest plants have the highest ratios (av. 91.07), while plants in ordinary forests and humid temperate regions exhibit intermediate values (av. 90.78), on the average slightly above the value for lacustrine plants. Further, aquatic plants growing in stagnant water have a higher ratio than those growing in nonstagnant water.

TABLE 15.—ISOTOPIC COMPOSITION OF CARBON FROM GRAPHITE AND CALCIUM CARBONATE (Wickman and von Ubisch, 1951)

Material	Source	C^{12}/C^{13}	Dif.
Calcite	Parainen, Finland	88.75	
Graphite	Parainen, Finland	89.17	0.42
Calcite	Crown Point, New York	88.80	
Graphite	Crown Point, New York	89.55	0.75
Limestone	Schwarzbach, Bohemia	88.82	
Graphite	Schwarzbach, Bohemia	90.35	1.53
Limestone	Amalia mine, Moravia	88.85	
Graphite	Amalia mine, Moravia	90.46	1.61
Graphite	Voitsau, Austria	90.71	—

Wickman concludes from these observations that "in places where the (carbon-dioxide) cycle cannot develop, *e.g.* in the open sea or in deserts, enrichment is much less than in places where the cycle is more complete and intense, *e.g.* in tropical rain forests or stagnant water."

The results on carbon that have been reported as C^{12}/C^{13} ratios are summarized graphically in figure 2. The ranges thus indicated for some types of materials are undoubtedly too great because they represent the results of different workers and thus show systematic differences of values because of differences in instrumentation. This is particularly true of the results on vegetable carbon, bituminous sediments, and graphite.

Craig (1953) briefly reviewed previous work

on carbon isotopes and reported the results of about 300 new determinations. He did not give absolute ratios but rather differences in per mil in C^{13}/C^{12} between the sample measured

For rapid rough comparisons the δ values expressed in per cent may be added to the standard ratio, and for small values of δ the result will not be far off. For $\delta = -10\%$, the

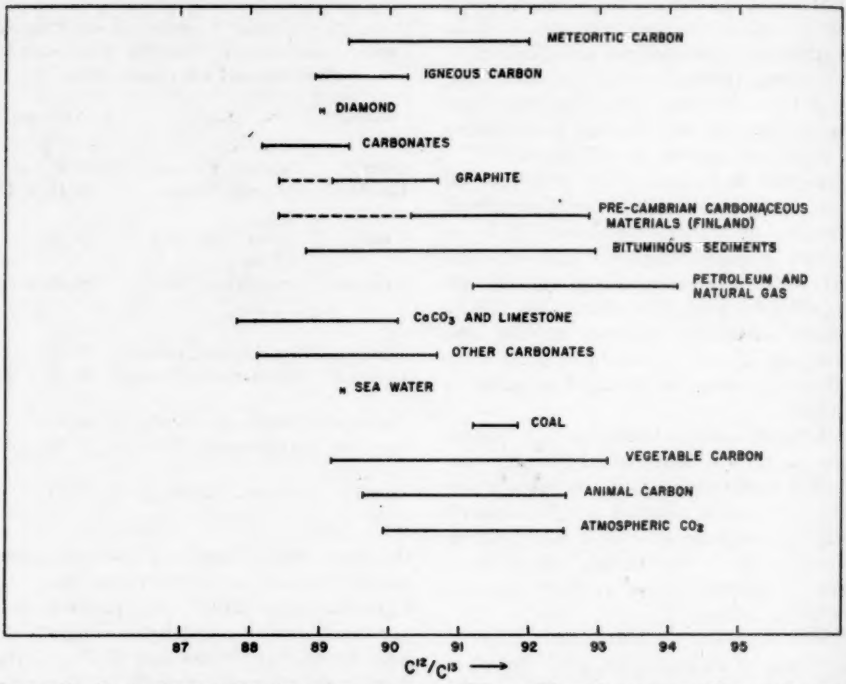


FIGURE 2.—CHART SHOWING RELATIVE ABUNDANCES OF C^{12} AND C^{13} IN CARBON FROM VARIOUS SOURCES

and a standard gas, which was carbon dioxide from a belemnite of Jurassic age, *Belemnitella americana*, from the Peedee formation of South Carolina. Measurement of differences from a standard is much more accurate as well as much more rapid than determination of absolute ratios; the modifications in technique described by Craig enabled him to measure variations in the isotope ratio to an accuracy of $\pm 0.01\%$ of the abundance of the isotopes. Using the same material measured by Nier (1950) and Nier's value of C^{13}/C^{12}, Craig (Personal communication) determined the C^{12}/C^{13} ratio of his standard to be 88.89. He gives the following equation for finding the C^{12}/C^{13} ratio of any of his samples from the value of δ:

$$C^{12}/C^{13}\ (\text{sample}) = \frac{88.89}{1 + \frac{\delta}{1000}}$$

C^{12}/C^{13} ratio calculated by this method is 89.89, whereas the true value from the equation is 89.79.

Figure 3 is a modification of Craig's chart, giving deviation from his standard in per mil. Even without changing his results to C^{12}/C^{13} ratios general comparisons with the work reported above are possible. A glance at the chart, for example, shows that his results confirm the previous indications that carbonates are high in C^{13}, that organic carbon is high in C^{12}, and that marine plants contain more C^{13} than land plants, as Wickman (1952) found. Marine invertebrates and plants are intermediate between carbonates and land plants. Ranges for these and carbons from other sources are shown in Table 16. Values are in per mil difference from C^{13}/C^{12} ratio of the standard gas, so negative values indicate higher C^{12}/C^{13} ratios.

Craig's values for atmospheric CO_2 indicate

a lower content of C^{13} than those previously reported. He recognizes that CO_2 collected near cities may have varying proportions of carbon from coal, wood, oil, etc., and plans to measure

Schubert (1947) studied the exchange of CO_2 between $BaCO_3$ and the atmosphere.

In the first determinations, they used precipitated $BaC^{14}O_3$ and $BaC^{13}O_3$ because the

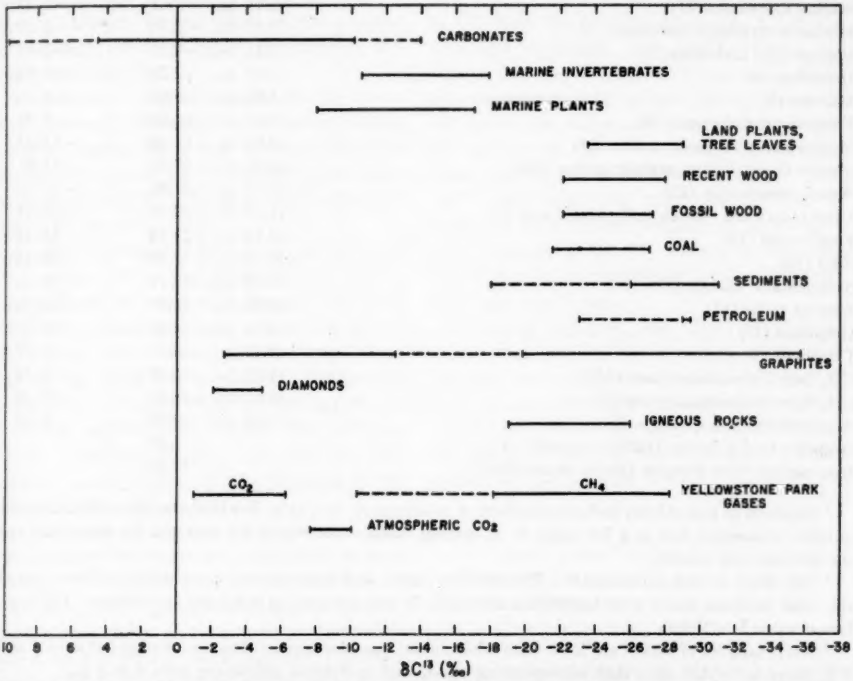


FIGURE 3.—CHART SHOWING DIFFERENCES BETWEEN C^{13} CONTENT OF CARBON FROM VARIOUS SOURCES AND THAT OF AN ARBITRARY STANDARD
After Craig (1953).

CO_2 from air collected over the ocean to obtain a better result.

Graphite from the Canyon Diablo meteorite is approximately 11‰ heavier than carbon of iron carbide of the same specimen. This fact should be taken into consideration in measuring the C^{12}/C^{13} ratios of meteorites and in interpreting the results of such measurements.

Additional results on C^{12}/C^{13} ratios in carbonates are given by Baertschi (1951a) in a paper in which O^{16}/O^{18} ratios are also given. (*See*, section on Oxygen.)

Exchange Reactions Involving Carbonates

In studies of the isotopic composition of carbon, especially in carbonates, it is important to know whether the ratio can be changed by exchange after the material was formed. In an attempt to answer this question Armstrong and

movement of the radiocarbon (C^{14}) is easily detected. They placed the $BaCO_3$ in covered Petri dishes and found that after 6 days it lost 2.7% of its activity, presumably by exchange of $C^{12}O_2$ of the atmosphere for $C^{14}O_2$ of the $BaCO_3$. Measurement of the activity was accurate to ±1.0 to 1.5% of the amount found. The postulated reactions are:

$$C^{12}O_2 + H_2O \rightarrow H_2C^{12}O_3$$
$$BaC^{14}O_3 + H_2C^{12}O_3 \rightarrow BaC^{12}O_3 + H_2C^{14}O_3$$
$$H_2C^{14}O_3 \rightarrow H_2O + C^{14}O_2 \uparrow$$

The evidence cited for this interpretation is twofold: (1) The $BaCO_3$ lost no radioactivity when it was protected from either CO_2 or H_2O, (2) the radioactive CO_2 lost to the air had the same amount of activity as that lost by the $BaCO_3$.

TABLE 16.—ISOTOPIC COMPOSITION OF CARBON FROM VARIOUS SOURCES (CRAIG, 1953)

Type of Material	δC^{13} (0/00)	Av.
Standard *Belemnita americana*	0.00	
Marine limestones (21)[1]	+2.44 to −33.3	−0.24
Marine-invertebrate carbonate (5)	+0.35 to −5.92	−2.15
Marine-algal carbonate (5)	+4.31 to −4.51	+2.01
Dolomites (6)	+2.65 to −2.29	+0.82
Marbles (5)	+3.06 to +0.63	+1.26
Fresh-water carbonates (9)	+9.82 to −14.10[2]	−2.28
Marine plants; organic carbon (11)	−8.06 to −17.05	−13.35
Marine invertebrates; organic carbon (10)	−10.66 to −17.86	−13.80
Wood; present-day (22)	−22.50 to −27.86	−25.36
Land plants and tree leaves[3]; present-day (13)	−12.15[4] to −29.08	−26.27
Fossil wood (15)	−22.45 to −27.34	−24.42
Coal (14)	−21.59 to −27.20	−24.48
Sedimentary[5] carbon (17)	−8.99[6] to −30.77	−26.96
Igneous rocks (11)	−18.98 to −25.95	−23.56
Graphites (15)	−2.73 to −35.46	−16.29
Diamonds (6)	−2.42 to −4.67	−3.37
CO_2 from Yellowstone gases (13)	−1.06 to −6.35	−2.82
CH_4 from Yellowstone gases (9)	−10.37[7] to −28.38	−25.30
Atmospheric CO_2, Chicago (5)	−7.36 to −9.94	−8.55
Graphite from Canyon Diablo meteorite (1)	−6.26	
Iron carbide from Canyon Diablo meteorrite (1)	−17.88	

[1] Numbers in parentheses indicate numbers of values given by Craig. For the most part this is also the number of samples, but in a few cases, *e. g.*, igneous rocks, some values are averages for more than one sample from one locality.

[2] This value is from carbonate in a Precambrian dunite and is not strictly comparable to the values of the other samples, which were travertines and tufas. It was not used in obtaining the average. The next-lowest value is −10.09.

[3] Seven samples of leaves are from trees whose wood was also studied. Leaves average between 1 and 2 ‰ lower in C^{13}/C^{12} ratio than corresponding wood, with individual differences from 0 to 2 ‰.

[4] Anomalous value not used in obtaining average. Next-lowest value −23.60.

[5] Bituminous and carbonaceous shales, bottom ooze, crude oil, and residual tar.

[6] This value is for "metamorphic chalk" which appears to be out of place in this group. It was omitted in obtaining the average. The next-lowest value is −14.04 and all of the others (except one, −17.98) are below −22.99.

[7] Anomalous value not used in obtaining average. Next-lowest value −20.64.

Similar experiments were tried with $BaCO_3$ containing 2.86 atom per cent excess C^{13} by exposing it to atmospheric $CO_2 + H_2O$ in a desiccator. The excess of C^{13} was reduced to 2.64, indicating that exchange with atmospheric CO_2 had taken place. At the end of the run the CO_2 in the desiccator was enriched in C^{13}, but no quantitative measurements could be made because of the great dilution.

The authors conclude that these observations indicate the necessity for keeping away from contact with CO_2 and H_2O carbonates that are to be used as isotope reference materials.

Yankwich (1948) reported that heating $BaCO_3$ produced samples that could be stored for long periods without serious loss of activity.

To check these findings of Armstrong and Schubert and of Yankwich, Samos (1949) performed several sets of experiments:

1. *Effect of relative humidity.* A sample was placed in a desiccator, with fixed relation to a counter, and counted in air. Then CO_2 was passed through the desiccator for 15 minutes, it was sealed for 2 hours, the CO_2 was swept out with air (CO_2 adsorbed 25 to 40% of the β-rays before they reached the counter), and the sample was counted again. Relative humidities of 3.2 to 75% produced a 1.2 to 1.5%

irregular decrease in the counting rate with a probable error, ±0.3%. On another batch of material, relative humidities of 18.8 to 75% produced decreases of 2.3 to 2.5% (probable error, ±0.5%). Conclusion: The amount of moisture present has no effect on the amount of exchange, at least when the relative humidity exceeds 3%.

2. Variations of almost tenfold in the *thickness of sample* produced no variation in the amount of exchange of a given batch of active $BaCO_3$. Conclusion: *All* crystallites in the material undergo exchange. Thickness studied varied from 0.56 to 4.44 mg/cm².

3. *Effect of heating.* Samos heated samples ½, 1, and 1½ hours at 140°C. The one heated for 1½ hours showed *no* exchange afterward; the others showed small and variable amounts. Heating an active sample in air caused it to lose 2.5 to 3.0% of its activity. Heating in vacuo or in nitrogen produced no loss in activity but stabilized the sample. The probable effect of heating is simply to increase the particle size to a point where exchange is no longer effective. (*See* 4, below.)

4. Effect of particle size. (a) Coarse material was prepared by dropwise precipitation over a 2-hour period near 100°C. This material showed *no* exchange. (b) Finer material precipitated at room temperature, when treated as described above, showed 1.75% loss in activity. (c) Very fine $BaCO_3$, precipitated rapidly from concentrated $BaCl_2$ and partly frozen Na_2CO_3 solution, lost 4.5% of its activity. Conclusion: The amount of exchange depends on the particle size, which indicates that the exchange takes place on the crystal surface.

5. *Time of contact with CO_2.* Runs of 1 to 15 minutes with the very fine material showed losses of activity from 1 to 4.1% (probable error, ±0.4%)—the longer the time of contact, the greater the loss. It approached the limiting value for this material (4.5%) in 15 minutes, which indicates that it reaches equilibrium quickly, and much longer runs are not necessary.

In the preliminary work of preparing active samples, Samos attempted to prepare an active solution of Na_2CO_3. No exchange took place. No exchange has been demonstrated, therefore, between solid carbonate and the $CO_3^=$ ion in solution.

Exchanges like those described above undoubtedly take place with C^{12} and C^{13} but at a different rate and to a different extent.

Haul, Stein, and Louw (1951) heated dolomite and calcite to 700°C. under a CO_2 pressure of 400 mm. The CO_2 had an abnormal content of C^{13}. After the runs the amount of C^{13} in the CO_2 had decreased. This could indicate exchange between CO_2 and carbonate, but could also be explained by partial decomposition of the carbonates and recombination of the resulting oxides with the C^{13}-enriched CO_2. The fact that dolomite showed more "exchange" than calcite did under the same conditions is an indication that this may explain at least a part of the change in the C^{13} content of the CO_2, since dolomite decomposes at a lower temperature than calcite does.

Arrhenius, Kjellberg, and Libby (1951) concluded that the $CaCO_3$ of pelagic shells in a core had not undergone significant exchange with bottom CO_2. The method was indirect; the temperature of formation of shells at various depths in the core was determined by the oxygen-isotope method:

Depth	*Temp.*
0–2 cm	21°C
10–11.5 cm	21°
20 cm	19.5°
200 cm	17.5°

They concluded that, since these are about the surface temperatures to be expected, any exchange that may have taken place is insignificant.

This conclusion might have been predicted from the work of Samos. Unfortunately, they do not give the particle sizes of their samples, but undoubtedly naturally occurring carbonates in shells, carbonate minerals and rocks, etc., are much coarser than the coarsest material that Samos worked with, so no significant amount of exchange would be expected, even in contact with moist air.

Nitrogen

General Statement

Many estimates of the isotopic abundance of nitrogen have been made, but little work has been done on this element on which geologic interpretations could be based. For the equilibrium

$$N^{15}H_{3(g.)} + N^{14}H_{4\ (sol.)}^{+} \rightleftarrows N^{14}H_{3(g.)} + N^{15}H_{4\ (sol.)}^{+}$$

TABLE 17.—ISOTOPIC COMPOSITION OF NITROGEN FROM PETROLEUM AND COAL (Smith and Hudson, 1951)

Material	Age (m.y.)	% N^{15}
Crude oil, Leduc No. 1, Alberta, Canada	Devonian (290)	0.3715 ± 0.0003
Crude, Lloydminster No. 3, Alberta, Canada	Lower Cretaceous (105)	0.3725 ± 0.0013
Coal, Atoka formation, Seminole, Okla.	Pennsylvanian (230)	0.3740 ± 0.0016
Coal, Frontier formation, Little Horse Creek, Wyo.	Cretaceous (70–110)	0.3687 ± 0.0002

Urey and Aten (1936) give $\alpha = 1.027$. For the same reaction, Thode, Graham, and Ziegler (1945, p. 46) give $\alpha = 1.031 \pm .002$ at 25°C.

N^{15}/N^{14} in Radioactive Minerals

White and Yagoda (1950) extracted nitrogen from radioactive minerals and measured its isotopic composition. There appeared to be a systematic variation with geologic age, but this has not been confirmed.

N^{15}/N^{14} in Coal and Petroleum

Smith and Hudson (1951) determined the N^{15}/N^{14} ratio of the nitrogen in oil and coal, with the results shown in Table 17. For comparison, they determined values of 0.3705 ± 0.0005 and 0.371 ± 0.002 for tank and atmospheric nitrogen. They concluded that the deviation is no greater than the probable overall reproducibility of the experiments, so no variation of N^{15} with age has been demonstrated for these materials.

Gravitative Separation of the Isotopes of Nitrogen

McQueen (1950) measured the per cent separation of the isotopes of nitrogen by comparing $N^{14}N^{14}/N^{15}N^{15}$ for a sample with the same ratio of N_2 from ground level (Table 18).

TABLE 18.—VARIATION OF ISOTOPIC COMPOSITION OF ATMOSPHERIC NITROGEN WITH ALTITUDE (McQueen, 1950)

Height (km.)	Date	% Separation*
55.4–58.8	7-21-49	3.9 ± 0.4
53.6–57.7	6-2-49	2.7 ± 0.3
49.0–59.8	7-26-48	2.7 ± 0.5
50.4–53.3	12-6-48	0.4 ± 0.3
48.8–47.6	8-30-49	0.8 ± 0.3
41.4–44.9	12-6-49	<0.3

* $[(N^{28}/N^{29})$ Samp.$-(N^{28}/N^{29})$ Ground$] \times 100 =$ % separation.

The observed separation was less than the calculated, which indicates stirring in the atmosphere, especially below 40 km.

OXYGEN

Relative Abundance of O^{16} and O^{18}

Many of the studies of O^{16}/O^{18} ratios have been made in connection with work on heavy water and are reported in the same articles that report H^1/H^2 ratios. Most of those results are recorded above under *Hydrogen*.

A great many studies of the isotope ratio in oxygen have been made. Bainbridge and Nier (1950) list 23 results obtained since 1929. The 10 that have been made since 1940 range from 480 to 525 and average 498 for the ratio O^{16}/O^{18}. They adopt the value of 489.2 ± 0.7 obtained by Nier (1950) on atmospheric oxygen. Bleakney and Hipple (1935) analyzed more than 100 samples from a variety of sources, including a few meteorites, and found that the results "clustered around 500". They showed that the value for tank oxygen varies from tank to tank.

Murphy (1941) also obtained a value of 500 for O^{16}/O^{18}. He reported 4.9 for O^{18}/O^{17}. The average value reported for this ratio is very close to 5.

Much of the early work on the isotopes of hydrogen was done by accurate density determinations on water prepared from the hydrogen, assuming that the oxygen used in the combustion was of constant composition. When it became evident that such was not the case, there was much interest in determining variations in the isotopic composition of oxygen in its common sources, the atmosphere and water.

A recent review by Dole (1952) covers not only the chemistry of the isotopes of oxygen, as indicated by the title, but also summarizes briefly the natural variations of the oxygen isotopes.

Standard Reference Materials for O^{18} Determinations

Tank oxygen is sometimes used in preparing water from hydrogen samples for density determinations. Smith (1934a) showed that tank oxygen is heavier than atmospheric oxygen and obtained differences of 1.4 and 2.4 γ in two runs. After an additional distillation the difference was 2.8 γ. The density, therefore, depends upon the history of a tank of oxygen, and in isotope work the isotopic composition of tank oxygen must be determined or the difference eliminated by using the same tank oxygen for an entire series of determinations including the *standard*.

Jones and Hall (1937) suggested an artificial standard with which to compare densities of waters from various sources, rather than using a natural standard, which may be subject to variation. Equilibrium is established rapidly at elevated temperatures, so standard samples could be prepared quickly. They equilibrated water vapor with excess air at 1800°A; the resulting water showed an increase in density of 7 γ.

Relation between Density and O^{18} Content of Water

As with hydrogen, several methods have been used in reporting the abundance of the isotopes of oxygen. Perhaps the two used most are density differences of the derived water and numerical evaluation of the ratio O^{16}/O^{18}.

Washburn, Smith, and Frandsen (1933, p. 458) give an equation relating atomic fractions of O^{17} and O^{18} to change of density. If we neglect O^{17} and the uncertainty factor, the equation simplifies to

$$P_{18} = 9.0094\Delta + 0.0016$$

where P_{18} = atomic fraction of O^{18} and Δ = difference in density (in γ) between the sample of water being studied (if it contains normal hydrogen) and ordinary water. The accepted value for O^{16}/O^{18} was about 630 when the equation was formulated. The constant 0.0016 must now be changed to 0.002, which brings the value of the ratio for $\Delta = 0$ (normal water) to 498. The equation then becomes

$$P_{18} = 9.0094\Delta + 0.002.$$

Figure 4 shows the relation between density and O^{16}/O^{18} ratio for water with hydrogen of normal isotopic composition. The values of O^{16}/O^{18} were calculated from assigned values of Δ, using the modified equation.

O^{18} in Water and in the Atmosphere

Morita (1936) reports that atmospheric oxygen contains more O^{18} than does that of water. In a paper with Titani (1936b), more details are given. They combined three samples of oxygen with a pure electrolytic hydrogen: (1) atmospheric oxygen, (2) the first 5% of oxygen derived by electrolysis of water, and (3) oxygen evolved after electrolysis of water was 95% complete. Water from (3) was 2 γ heavier than that from (2), indicating an isotopic separation factor of 1.01 for electrolysis of water. Water from (1) was some 8 γ heavier than that from (3), indicating that atmospheric oxygen is about 4% richer in O^{18} than is oxygen of normal water. The distribution coefficient between air and water for O^{18} is therefore 1.04. Urey and Greiff (1935, p. 325) give a calculated value of $\alpha = 1.020$ for this coefficient at 25°C.

Dole (1936a) measured the density of water prepared from atmospheric oxygen plus tank hydrogen and from oxygen of Lake Michigan water plus the same tank hydrogen. The water from atmospheric oxygen was 6 γ heavier. Dole says that this can be explained by assuming an isotopic exchange equilibrium between H_2O and O_2 at -50°C in the lower part of the stratosphere. The calculated separation of the isotopes of oxygen by gravity is not sufficient to explain the observed excess O^{18} in the atmosphere near the surface of the earth.

Using purified Lake Michigan water as a standard, Dole (1936b) obtained a value of $+1.5$ γ for purified Atlantic Ocean water and -1.95 γ for water condensed artificially from the atmosphere. He demonstrated, by electrolyzing the waters and recombining the derived oxygen samples with the same tank hydrogen,

that the variations in density are due primarily to variations in the O^{16}/O^{18} ratio.

Later Dole (1949) and Roake and Dole (1950) elaborated upon the exchange equilibria that could produce enrichment of O^{18} in atmospheric oxygen. Experimental work demonstrated the reality of the exchange between CO_2 and O_2 in the electric discharge but did not produce measurable reaction between H_2O and O_2. Roake and Dole emphasize that the $CO_2 + O_2$ reaction is a random (not at equilibrium) exchange. They point out that their results do not preclude the possibility of a slow (equilibrium) exchange between H_2O and O_2 that could explain a part, or all, of the excess O^{18} in the atmosphere.

Dole (1949) mentioned other equations that may play a part in the process but indicated that the irreversible reaction $CO_2^{18}(g) + O_2^{16}(g) \rightarrow CO_2^{16}(g) + O_2^{18}(g)$ is probably the one that actually brings about the enrichment. If this process is operative in the stratosphere there remains the problem of whether, and how, the oxygen thus enriched in O^{18} can be transferred from the stratosphere to the earth's surface.

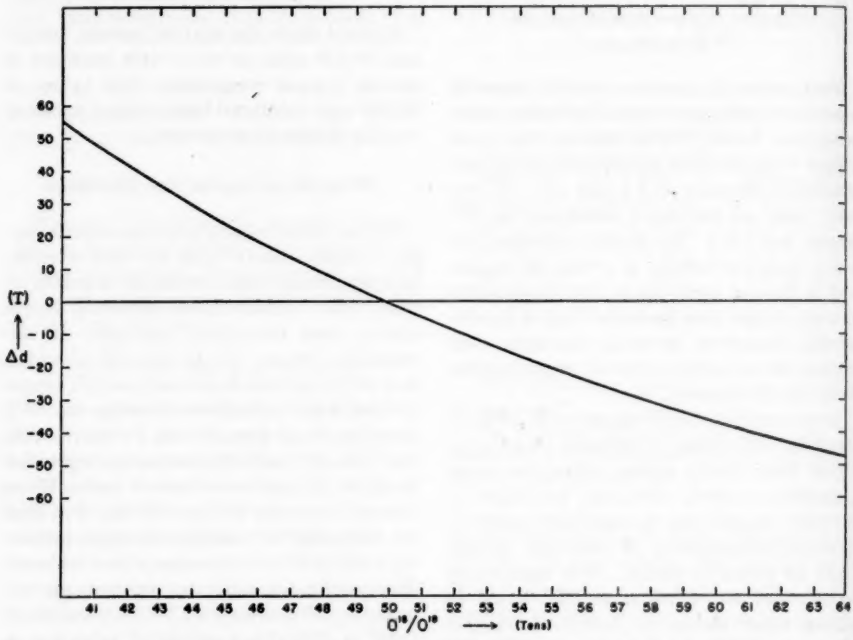


FIGURE 4.—GRAPH SHOWING RELATION BETWEEN O^{16}/O^{18} AND THE DIFFERENCE IN DENSITY BETWEEN NORMAL WATER AND WATER PREPARED BY COMBINING A GIVEN SAMPLE OF OXYGEN WITH HYDROGEN OF NORMAL ISOTOPIC COMPOSITION

Rakestraw, Rudd, and Dole (1951) suggest that the high O^{18} content of the atmosphere might be explained, at least in part, by addition of oxygen to the atmosphere from the zone at a depth of about 550–950 m in the ocean, where the dissolved oxygen is enriched in O^{18}. However, they suggest no mechanism whereby this might take place.

Dole and Rudd (unpublished data, quoted by Dole, 1952, p. 296) studied the isotopic composition of atmospheric oxygen from many parts of both North America and South America. They found no differences in O^{18} content greater than 0.00015 percentage unit, which is approximately equivalent to 0.15 γ in water density.

O^{18} in CO_2 and in Photosynthetic Oxygen

Webster, Wahl, and Urey (1935) studied the reaction $2H_2O^{18} + CO_2^{16} \rightleftarrows 2H_2O^{16} + CO_2^{18}$ and obtained values of K = 1.097 and α = 1.047 at 0°C, indicating concentration of O^{18} in the CO_2. Experiments confirmed the expected fractionation.

Greene and Voskuyl (1936) found the O^{18} content of CO_2 higher than that of H_2O. Assuming that there is no discrimination between oxygen from CO_2 and H_2O in photosynthesis, they calculate that oxygen given off by plants shou d produce water 6.8 γ heavier than normal water. They suggest that this may be the explanation of the 6 γ anomaly reported by Dole for atmospheric oxygen, but later work appears to invalidate this hypothesis.

Vinogradov and Teis (1941) determined the O^{18} content of photosynthetic oxygen to be more nearly like that of H_2O than of atmospheric oxygen. They point out that, to explain the isotopic composition of atmospheric oxygen, not only plant sources must be considered, but also equilibrium reactions with CO_2 and water vapor of the atmosphere under the influence of ultraviolet radiation and electric discharges. (Also cosmic radiation?)

Ruben *et al.* (1941), using O^{18} as a tracer, demonstrated that oxygen evolved in photosynthesis is identical in isotopic composition to the oxygen of the water used by the plants rather than that of the carbon dioxide. This confirms the results of Vinogradov and Teis, but the times of publication of the two papers were so nearly identical that neither paper mentions the other.

Dole and Jenks (1944) made a number of determinations of the density of photosynthetic oxygen from plants. The quantity Δ d ranged from 0.6 to 1.8 and averaged 1.16 γ. Oxygen from the CO_2 gave water with Δ d of 8.2 γ so these results confirm earlier findings that photosynthetic O_2 is derived essentially from the water used by plants.

Vinogradov (1947) confirms the identity of isotopic composition of photosynthetic oxygen with that from water. He disagrees with Dole and insists that exchange equilibria between H_2O, CO_2, and O_2 (in the biosphere) will decrease the weight of gaseous oxygen, not increase it. He suggests that the excess O^{18} of the atmosphere may be explained by a process that is more or less the reverse of photosynthesis. That is, as material is decomposed and oxygen freed to the atmosphere, there may be a preferential binding of O^{16} in compounds so that the released oxygen becomes richer in O^{18} until an equilibrium value is reached.

O^{18} in Carbohydrates

Morita, Goto, and Titani (1938) studied the isotopic composition of carbohydrates.

(1) In one series of experiments they burned carbohydrates in atmospheric oxygen and determined the density of the water thus produced:

Substance	Δd_S	$\Delta d_{O^{18}}$	Δd_D
Sugar	7.4γ	6.0γ	1.4γ
Cotton	6.7	5.0	0.7
Wood	4.5	3.4	1.1

(2) In a second series they burned sugar with electrolytic oxygen and obtained Δ d_S = 0.6 γ, Δ $d_{O^{18}}$ = − 0.2 γ, and Δ d_D = 0.8 γ.

(3) Reaction of sugar with hydrogen produced water that in three experiments gave Δ $d_{O^{18}}$ = 3.9, 5.6, and 4.4 γ; average = 4.6 γ.

(1) and (2) show clearly that oxygen of the atmosphere is heavier than that of water by some 6 γ. It also indicates excess density of the hydrogen of sugar of about 1 γ, although this value is less certain, being much nearer the limit of experimental error. The authors attribute this difference to exchange equilibrium between sugar and water, by which sugar is slightly enriched in H^2.

(3) indicates that the oxygen of sugar is some 5 γ heavier than oxygen of water. They offer the explaantion that heavy oxygen is probably fixed in plants from carbon dioxide. However, they assume that photosynthetic oxygen contains as much O^{18} as does the atmosphere (7 γ), so their calculations of the amount of oxygen of plants derived from CO_2 is probably in error.

They converted only 62 to 73 per cent of the oxygen of the various samples to water, so another possible source of error is isotopic fractionation during the reaction.

Teis (1950a) reacted carbohydrates with hydrogen in the same manner. The resulting water was electrolyzed, and the oxygen pro-

duced recombined with standard hydrogen; the standard water was given identical treatment, which eliminated any isotopic anomalies in the reactive hydrogen. He obtained the following results:

Material	% O_2 as H_2O	$\Delta d O^{18}$
Glucose (lab. prep.)	97	11.2γ
Glucose, corn	92	10.8
Glucose, corn	75	10.1
Absorbent cotton	~100	10.0
Absorbent cotton	~100	10.7

Teis started with the knowledge, not available to Morita and his coworkers, that photosynthetic oxygen has the same composition as that of normal water. He assumed, therefore, that the oxygen fixed in plants comes essentially from the CO_2 taken in and that this oxygen should show a density anomaly about the same as that of the CO_2 (11 γ). The results given in the table confirm this prediction; the average of the five results reported is 10.56 γ.

O^{18} in Hot Springs and Fumaroles

Dole (1936c) determined the density of water from three hot springs in Nevada to be 2.8 γ ± 0.6 γ lighter than Lake Michigan water. All three springs were the same. He electrolyzed the Nevada and Michigan waters and recombined the resulting oxygen samples with tank hydrogen. The hot-spring water was still 2.2 γ lighter, showing that most of the difference is due to lower O^{18} content, not H^2.

In the same paper, Dole reported that melted snow from an altitude of 6,000 feet near Reno appeared to be intermediate in density between Lake Michigan water and the water from Nevada hot springs. The difference in density is not reported, because the sample gave out before its density was determined exactly.

Friedman (In press) quotes unpublished results of Epstein on the oxygen of water from a fumarole at Parícutin. It is some 2 γ heavier than normal water. Silverman (1951, p. 28) obtained about this same value for oxygen from the Parícutin lava, which indicates that there was probably high-temperature equilibration between the water and the silicates.

O^{18} in Minerals, Rocks, and Meteorites

There has been a great deal of interest in the isotopic composition of the oxygen in minerals and rocks, but little systematic interpretative work has yet been done. Manian, Urey, and Bleakney (1934) determined the O^{16}/O^{18} ratio for three stony meteorites, a granite from Maine, and laboratory potassium chlorate. The precision of the measurements was not high, and all the samples gave the same result within their experimental error. The value of the ratio was determined as 514 ± 13.

Even after the methods had been refined a great deal, Urey (1951) reported that the isotopic composition of oxygen from meteorites is practically identical with that of oxygen from igneous rocks.

Dole and Slobod (1940) determined the isotopic composition of oxygen from several carbonate rocks and a few iron ores. Modern clam shells, limestone and dolomite of Pennsylvanian age, Niagara limestone, and marble of the Grenville series all gave essentially the same results, +9.2 γ, for water prepared from their oxygen, with respect to Lake Michigan water. Experimental error is given as ±0.1 γ.

Oxygen from marble of the Grenville liberated as CO_2 by acid gives water of 9.2 γ; released thermally, 7.9 γ. The authors attribute the difference to isotopic fractionation when the carbonate is decomposed by acid. They say that the 7.9 γ can be explained quantitatively by the isotopic exchange equilibrium theory of Urey and Grieff. More details are given in the original dissertation by Manian. Results on individual specimens ranged from 489 ± 5 to 540 ± 9.

Oxygen from iron ores of Keewatin and Huronian age does not differ significantly in its isotopic composition from that of normal water. Slight excess density of oxygen from oölitic (3.5 γ) and fossil (4.5 γ) ores of Silurian age is probably due to the presence of carbonate in the ore.

Thode (1949) reports that the oxygen of Swedish magnetite has the same isotopic composition as oxygen from Lake Ontario water.

Hall and Hochandel (1940) reduced cuprite from Bisbee with commercial electrolytic hydrogen and found the water thus formed to be 5.5 γ lighter than water prepared from the

same hydrogen and atmospheric oxygen. This shows the oxygen of the cuprite to be about the same as that of water, suggesting that the mineral was formed by the action of water rather than air on the primary copper sulfides.

TABLE 19.—DENSITY OF WATER PREPARED FROM OXYGEN OF OXIDE MINERALS (Vinogradov and Dontsova, 1947a)

Mineral	Locality	% O_2 freed	$\Delta d_{O^{18}}$
Cuprite	Nizhn. Tagil, Gumash mine	100	0.0γ
Magnetite	Blagodat' Mountain	90	5.4
Magnetite	Blagodat' Mountain	82	5.2
Magnetite	Blagodat' Mountain	85	6.0
Magnetite	Blagodat' Mountain	90	6.0
Chromite	Aktiubinsk region, Almazn mine	70	2.5

Vinogradov and Dontsova (1947a) found that oxygen from a modern mollusk (*Unio pictorum*) and from a carbonate rock from Lak'hmataia, Il'mensk Mountains, Urals, supposed to be of magmatic origin, produced water 7.8 and 6.5 γ, respectively, heavier than normal water. These anomalies are approximately the same as those obtained with oxygen of ordinary limestone.

They reduced cuprite, magnetite, and chromite with hydrogen at 600 to 1,300°C (Table 19).

The authors believe that the variability may be explained by the difference in the manner of origin of the various minerals—*i.e.*, whether they were formed from aqueous solutions, or out of contact with moisture, etc. They do not, however attempt specific correlations for the minerals studied.

Dontsova (1948), by oxidizing iron in the presence of (1) normal water and atmospheric oxygen, (2) normal water and oxygen enriched in O^{18}, and (3) normal oxygen and water enriched in O^{18}, showed that most of the oxygen going into the iron oxides was derived from the water. Later (Dontsova, 1950) he studied the isotopic composition of oxygen from oxide minerals by combining it with standard hydrogen. The water formed from the oxygen of limonite and hydrogoethite showed normal density; that from oxygen of magnetites in limestone contact zones from 10 localities averaged 5.0 γ heavier than normal water. From these data it is inferred that the oxygen of the limonite and hydrogoethite was derived from groundwater; that of the magnetite, at least largely from the limestone.

Vinogradov and Dontsova (1952) simulated the conditions of formation of contact magnetite by passing $FeCl_2$ and $FeCl_3$ vapor through crushed limestone at temperatures of 200° to 750°C. The oxygen of the magnetite formed was enriched in O^{18} by 7.5 γ, indicating that it was derived from the limestone. Magmatic titanomagnetite contained oxygen of normal isotopic composition. Vinogradov and Dontsova suggest that it should be possible to distinguish any oxygen-containing skarn mineral from its sedimentary or magmatic counterpart on the basis of the enrichment of the skarn minerals in O^{18}.

Teis (1950b) prepared water from the oxygen of a stalactite, limestone of a salt lake, and marine limestone. The samples gave density anomalies of 6.8, 7.0, and 8.1 γ with respect to a standard prepared from the same hydrogen used in the preparation of water from the carbonates. This is in good agreement with previous results on limestones. Presumably all these calcites were formed below 25°C. Probable error for all determinations is ±0.4 γ.

Ground waters from the Caucasus give values of 1.3 to 2.0 γ; a thermal spring, 2.4 γ. These values are near those reported for ocean water, 1.5 to 2.0 γ.

Carbonates deposited at higher temperature, even from water of the same isotopic composition, should have less O^{18}. Teis studied several carbonates from hot springs (Table 20). In accord with theory, there is less O^{18} in these carbonates than in those formed at lower temperatures.

Two calcites from Irkutsk, however, supposed to be of magmatic origin and therefore of much higher temperature of formation, gave values of 5.6 and 6.0 γ, almost as high as those formed around 25°C. Teis remarks that Vinogradov and Dontsova (1947a) obtained comparable results (7.8 and 6.5 γ) on similar material, but he offers no explanation of the apparent anomaly. Possible explanations are (1) the carbonate is not magmatic, but water-laid limestone that

has been caught up and metamorphosed; (2) if the carbonate is magmatic, it may have crystallized from an essentially anhydrous melt and thus have no close relation to the other carbonates studied by Teis.

TABLE 20.—DENSITY OF WATER PREPARED FROM OXYGEN OF CARBONATE MINERALS (Teis, 1950b)

Mineral	Locality	Prob. T of form.	$\Delta d_{O^{18}}$
Calcite	Podolak	~200°C	4.0γ
Calcite	Kastel', Crimea	~200	3.5
Calcite	Tadzhik, SSR Mandantag	200–300	2.5
Calcite	Shishim Mts., Urals	~200	3.6
Dolomite		~180	3.5

Teis believes that these density methods should provide an estimate of the temperature of formation of low-temperature carbonate (limestone, sedimentary dolomite, etc.) to about 7° or 8°C; of hot-spring and some hydrothermal carbonate to within 12° to 13°C.

Urey and his coworkers have been able to do much better than this, at least for limestones and related carbonates, by mass spectrometric methods. (*See* the summary of their work, below.)

It is much more difficult to decompose silicate minerals and rocks and collect their oxygen for study than to perform the same operation on water, organic material, or carbonates. Vinogradov and Dontsova (1947b) appear to have been the first to study silicates in this manner. They studied the isotopic composition of the oxygen of aluminosilicate rocks. The rocks were powdered, mixed with powdered graphite and heated to 1,700°–2,000°C in graphite crucibles in an induction furnace. The CO thus formed was treated with hydrogen to form water, which was compared with a standard prepared from the same hydrogen (Table 21). This method is said to free all the oxygen from the silicates.

The average O^{18} content of the rocks is the same as that of normal water, within experimental error.

Conclusions: (1) There is no fractionation of oxygen isotopes between water and primary aluminosilicates. (2) The observed differences are characteristic of the outer part of the lithosphere and of the biosphere.

Baertschi (1950a) made a much more systematic and comprehensive study of the isotopic composition of the oxygen in silicate rocks. He

TABLE 21.—DENSITY OF WATER PREPARED FROM OXYGEN OF IGNEOUS ROCKS (Vinogradov and Dontsova, 1947b)

Rock	Locality	av. $\Delta d_{O^{18}}$
Granite	East shore, L. Onega, Russia	±0.4γ
Basalt	Ballarne Schonen, Sweden	+0.8
Trap rock	Tulun area, Eastern Siberia	+0.8
Dolerite	Dalmeny Linlitghow, Scotland	−2.4

decomposed the samples with chlorine trifluoride and hydrogen fluoride. The reaction with silica, for example, would be:

$$ClF_3 + HF + SiO_2 \xrightarrow[20\ hrs.]{Pt,\ 430°C} O_2 + SiF_4 + HCl$$

Very nearly 100 per cent yields were obtained. The oxygen was pumped off, purified, and compared with a standard obtained from a Precambrian gneissic granite from South Dakota. The results are given (Table 22) in parts per mil deviation from the standard (positive values indicate more O^{18} than in the standard).

The average igneous rock is −2.0; the average sedimentary rock, +8.4. Clastic sedimentary rocks average +4.4; precipitated ones, +18.5. Sedimentary rocks pick up heavy oxygen from water as they are formed from igneous rocks; the finer clastics and precipitates pick up more than do coarse clastics. For diatomite K = 1.03 at 15°C.

There was probably no isotopic fractionation when the earth's crust was molten, so the average for basalt and similar rocks (−2.0) should be about the value for primordial water vapor and molten silicates. Sea water is −8.5, which is a decrease of 6.5 from the original value. Sediments and sedimentary rocks, according to Pettijohn (1949), contain an aggregate of oxygen about equal to that in the hydrosphere, so the oxygen of sedimentary rocks should show an increase of 6.5. The present

value, therefore, should be $-2.0 + 6.5 = 4.5$, which is very near the value obtained for clastic rocks.

TABLE 22.—ISOTOPIC COMPOSITION OF OXYGEN FROM VARIOUS SOURCES (Baertschi, 1950a)

	$\Delta O^{18}/O^{16}$ ‰
Igneous rocks:	
Gneissic granite, South Dakota (standard)	0.0
Basalt from Greenland (contains Fe + Pt metal)	−4.5
Obsidian (Iceland)	−4.5
Basalt (Oregon)	−1.5
Lava of Recent age (Etna, Sicily)	−1.5
Lava of Recent age (Parícutin, Mexico)	−0.5
Lava of Recent age (Hawaii)	−1.5
Sedimentary rocks	
Wishart quartzite (Precamb., Labrador)	+7.0
Cheshire quartzite (L. Camb., Vermont)	+2.5
Potsdam sandstone (U. Camb., Wisconsin)	+4.0
Arkose (Triassic, Connecticut)	+2.0
Shale (U. Ordovician Iowa)	+6.5
Flint (Cretaceous, Dover, England)	+15
Diatomite (Miocene, California)	+22
Meterorites:	
Tektite (Java)	+1.0
Moldavite (Hungary)	+3.0
Darwin glass (Australia)	+7.0
Miscellaneous:	
Fresh water (Lake Michigan)	−12.5
Sea water (Hawaii)	−8.5
Tank oxygen (from air)	+23

Probable error, ±1.5 ‰ of the ratio.

The abundance of O^{18} appears to decrease with increasing depth in the crust (Oana, 1942a), but there are as yet too few determinations to establish a correlation.

Baertschi (1950a) suggests that an important application of O^{18} content of silicate rocks is the possibility of distinguishing between orthoigneous rocks and igneous-looking metasedimentary rocks. He also suggests that magmatic water is some 10 per mil richer in O^{18} than sea water.

Baertschi and Silverman (1951, p. 318–326) give details of the chlorine trifluoride and fluorine methods of extracting oxygen from silicates. They conclude that the fluorine method, as now perfected, gives a higher and more consistent yield than the other, with no no indication of isotopic fractionation during the procedure.

TABLE 23.—ISOTOPIC COMBINATION OF OXYGEN FROM SILICATES (Baertschi and Silverman, 1951)

Material	$\Delta O^{18}/O^{16}$ (‰)
Olivine basalt	−1.6
Disco basalt	−4.4
Orthoclase from Randville pegmatite	+3.7
Vein quartz	+2.6
Eucrite	−0.2
Garnet schist	+5.2

Probable error ±0.1% of ratio

They repeated runs, by both methods, on some of the materials previously reported by Baertschi, and on some new samples. They used a different oxygen standard for which the O^{18} content is not given, so the only way to compare these results with Baertschi's is to obtain a factor from the samples common to both groups of data and apply it to the new samples. When this is done the results of Table 23 are obtained for the additional materials. The results obtained by the chlorine trifluoride method were used in deriving these values from those reported by Baertschi and Silverman because Baertschi used that method in the work summarized above.

They conclude that natural silicates vary as much as 2.4% in their O^{18}/O^{16} ratios.

Silverman (1951), using the fluorine-hydrogen fluoride method, extended the work on oxygen isotope ratios in silicates (Table 24). He repeats results on 14 rocks previously reported by Baertschi and by Baertschi and Silverman, and adds results on 10 more rocks. Other results on special problems are given in separate tabies. The reference oxygen used was from purified sea water from Hawaii. It was 8.5 ‰ lighter than the standard previously used, so 8.5 units must be subtracted from each value in Table 24 to make it comparable with those given in Tables 22 and 23. Even then they are not strictly comparable because they were obtained by different methods that do not give identical results.

Silverman points out that the results show almost perfect correlation between per cent of precipitated silica in siliceous sedimentary rocks and deviation of the O^{18}/O^{16} ratio from that of the standard.

TABLE 24.—ISOTOPIC COMPOSITION OF OXYGEN FROM VARIOUS SOURCES (Silverman, 1951)

Material	$\Delta O^{18}/O^{16}$ (‰)
Chicago tap water	−3.2
Hawaii sea water	0.0
Columbia River basalt	6.4
Disco basalt	6.6
Mount Etna lava	6.7
Dunite	6.8
Olivine basalt	7.0
Obsidian from Yellowstone	7.7
Gneissic granite	7.9
Nepheline syenite	8.3
Parícutin lava	8.5
Cheshire orthoquartzite	10.2
St. Peter sandstone	10.9
Arkose	11.4
Basal breccia	13.2
Quartz vein	14.0
Brazil quartz	14.0
Grafton orthoquartzite	14.7
Wishart orthoquartzite	15.1
Potsdam sandstone	15.5
Maquoketa shale	15.5
Atmospheric oxygen	19.2
Dover flint	29.3
Diatomite	30.3

Average deviations O^{18}/O^{16} ratios, <0.5 ‰.

From the results on diatomite, assumed to have precipitated at 15°C, and on quartz from Brazil, probably formed at about 200°C,[5] Silverman calculated the temperature coefficient of the fractionation factor for the silica-water equilibrium. The values are 1.030 and 1.014 at 15°C and 200°C respectively, so the change per degree centigrade would be −0.086 ‰.

Oxygen from two stony meteorites gave values of 6.3 and 6.5 ‰ above the standard; a moldavite and tektite, 10.4 ‰ each. The values for the stony meteorites fall within the range of basalts and similar rocks taken to represent the primordial (isotopic) composition for the planet. The moldavite and tektite fall within the range for clastic sedimentary rocks, which is interesting in view of the fact that these materials are chemically similar to certain argillaceous sediments.

TABLE 25.—VARIATION IN ISOTOPIC COMPOSITION OF OXYGEN ACROSS AN IGNEOUS CONTACT (Silverman, 1951)

Material	$\Delta O^{18}/O^{16}$ (‰)
Gabbro	6.1
Intermediate rock	7.7
Intermediate rock	8.4
Contact rock	8.7
Granophyre	9.0
Granophyre	9.9

Silverman says that these analyses do not provide any evidence for or against the extraterrestrial origin of tektites. The ratios found for stony meteorites, however, do support the notion that the structure and composition of all the planetary bodies of the solar system are similar. Further, McKellar (1949) concluded, on the strength of isotopic shifts in the band spectra of M-type stars, that the relative abundances of oxygen isotopes in stellar atmospheres is not significantly different from the values obtained from terrestrial materials.

Silverman selected a series of six samples, in a lateral extent of 20 feet, across the contact of a gabbro and an intruding granophyre. The samples, in order from unaltered gabbro to pure granophyre, gave the following values shown in Table 25. The granophyre is supposed to be of filter-press origin and so could not have melted or assimilated any of the gabbro. The variation cannot be due to crystal settling, because the section studied is horizontal, nor can it be due to direct crystallization of a silicate melt. The regular increase in the O^{18}/O^{16} ratio across the contact indicates to Silverman that the formation of the zone involved the transfer of material by some process of permea-

[5] Silverman used a value of 140°C, but he neglected to add the corrections for pressure given in Ingerson's (1947, p. 387) original article in which temperatures of formation of quartz crystals from Brazil were estimated by means of liquid inclusions. Silverman obtained a value of −0.128‰ per degree centigrade for the temperature coefficient of the fractionation factor.

tion, solution, or diffusion in a solid. This interpretation appears to be supported by a study of the texture of the zone, which shows idiomorphic crystals, transection of some crystals by others with no evidence of displacement

TABLE 26.—VARIATION IN ISOTOPIC COMPOSITION OF OXYGEN WITH INTENSITY OF METAMORPHISM (Silverman, 1951)

Specimen	$\Delta O^{18}/O^{16}$ (‰)
Olive-gray slate, No. 18	15.4
Black phyllite, No. 22	12.1
Black phyllite slate, No. 20	15.7
Garnet shist, No. 19	12.7
Chlorite schist, No. 30	12.5
Biotite-garnet schist, No. 28	12.9

or deformation, and other criteria for replacement.

The fact that the partially metamorphosed Cheshire quartzite shows less O^{18} (0.7 ‰) than the St. Peter sandstone suggests to Silverman that metamorphism may result in a decrease in O^{18} content. In an attempt to check this possibility, he studied a series of six specimens collected along a line normal to the northeast-southwest axis of a geosyncline in the Dutchess County, New York, metamorphic sequence. The intensity of metamorphism increases from west to east (Balk, 1936, p. 700), and in Table 26 the specimens are arranged in that order, except for No. 22, which was collected along the strike about 5 miles northeast of No. 18. There is no consistent trend, but the three higher-rank rocks do average a little lower in O^{18} than the others, which is in the right direction to support the suggestion that metamorphism decreases O^{18} content. Until much more work is done and the factors involved are evaluated much more carefully, it must remain a suggestion. Silverman recognizes this and says that in no case has his investigation been "sufficiently exhaustive to preclude the possibility of erroneous conclusions."

Baertschi and Schwander (1952) review very briefly the ClF_3 + HF and F_2 + HF methods of freeing oxygen from silicate rocks for isotope determinations. Then they outline another method much less complicated and expensive. Finely powdered sample is mixed with an excess of spectrographic graphite. The mixture is placed in a graphite boat in a gas-tight pyrex vacuum furnace and degassed at 1000°C and 10^{-4} mm pressure. The temperature is then

TABLE 27.—ISOTOPIC COMPOSITION OF OXYGEN FROM SILICATE ROCKS (Baertschi and Schwander, 1952)

Sample	R/R (‰)
Lamprophyre	−3.3 ± 0.3
Granite	−2.8 ± 0.2
Obsidian (Iceland)	−8.8 ± 0.4
Piedmontite schist	+10.8 ± 0.9
Siliceous sinter (Yellowstone)	+4.4 ± 0.2

raised to about 2000°C, and the oxygen of the sample is converted to CO, which is passed through a double collector mass spectrometer to compare its O^{18}/O^{16} ratio with that of a standard sample.

The first evolved CO was up to 2 ‰ (of the O^{18} content) poorer in O^{18} than the last part. This uncertainty, however, does not exceed ±0.3% of the O^{18}/O^{16} ratio.

The results are reported as $\Delta R/R$ in per mil, where R is the O^{18}/O^{16} ratio of the standard CO, and ΔR is the difference between this ratio and that of the sample (Table 27).

This method of freeing oxygen from silicates is very similar to the one described by Vinogradov and Dontsova (1947b), but the subsequent method of isotope measurement is entirely different from theirs.

Baertschi (1951a) published a preliminary account of the determination of O^{16}/O^{18} and C^{13}/C^{12} ratios on the same samples of some 150 carbonate rocks. The results are shown in Figure 5, with deviations of the ratios O^{18}/O^{16} and C^{13}/C^{12} from those of a standard limestone plotted in parts per mil as abscissae and ordinates respectively[6]. Negative values indicate

[6] Baertschi's standard is +2.34‰ with respect to the one used by Craig (1953), so by subtracting this amount from each of his C^{13}/C^{12} values the results can be compared directly with Craig's and calculations of C^{13}/C^{12} ratios can be made by using the equation given above in the discussion of Craig's work. Wickman's standard (C^{12}/C^{13} = 89.5) would be located on Baertschi's diagram at −14.0 (O^{18}) and −14.0 (C^{12}). Baertschi's standard has C^{12}/C^{13} = 88.25.

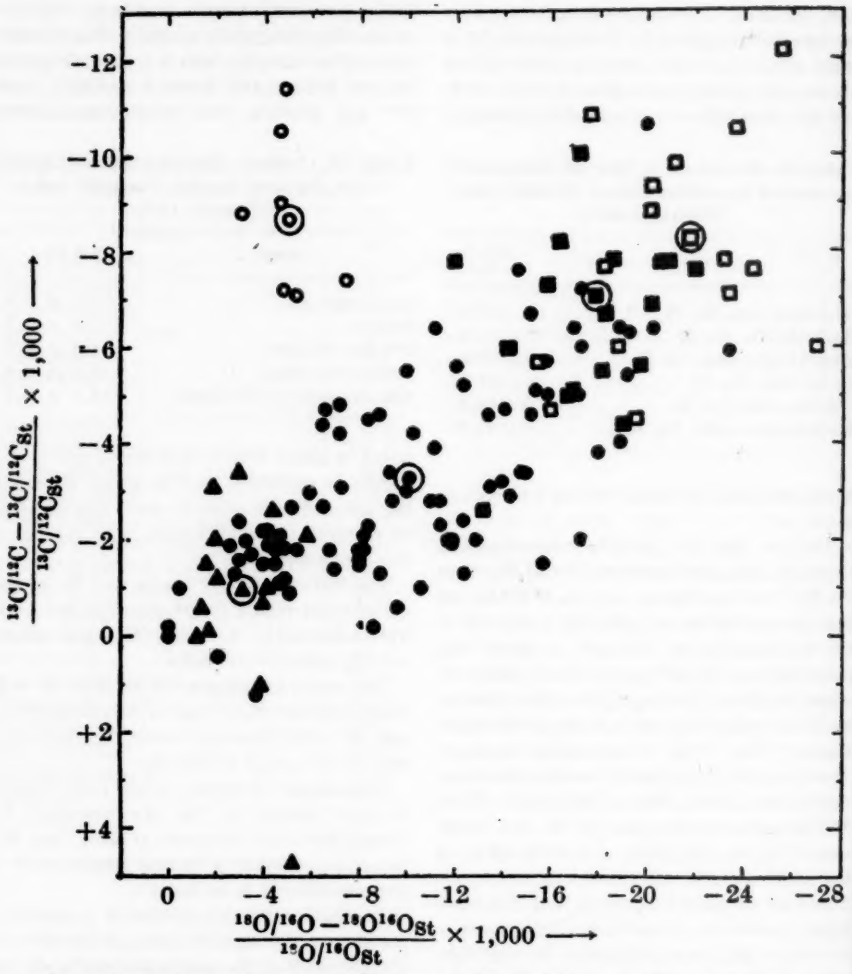


FIGURE 5.—RELATIVE ABUNDANCE OF OXYGEN AND CARBON ISOTOPES IN CARBONATE ROCKS

After Baertschi (1951), by permission of the Editors of Nature.

Triangles, sedimentary limestones (14); filled circles, metamorphic limestones (90, mainly from the Swiss Alps); filled squares, carbonatites (20, from Alnö, Uganda, South Africa, and Colorado); open squares, calcite crystals from Alpine veins cut by the Simplon tunnel (12); open circles, calcareous sinter precipitated from fresh water (7). Circled symbols give the average isotopic compositions of the different groups.

less of the heavy isotope in the sample than in the standard.

A glance at Figure 5 shows that a sample high in O^{18} is very likely to be high in C^{13} also, which indicates that the isotopes of oxygen and carbon are fractionated qualitatively the same way by most processes involving carbonate ions and carbon dioxide.

The average values for sedimentary limestones, metamorphic limestones, carbonatites, and calcite-bearing veins (circled points in Fig. 5) fall practically on a straight line, with the sedimentary limestones highest in the heavy isotopes and the vein carbonates lowest. These relations might have been predicted from Urey's demonstration (1948) that carbonates formed

at low temperatures are enriched in O^{18}, except that the relation between carbonatites and vein carbonates might not have been clear because of uncertainties as to their relative temperatures of formation. Baertschi's results indicate that the vein carbonates have, on the average, higher temperatures of formation. He ascribes the very low C^{13} content of the calcareous sinters (precipitated from fresh water) to the presence of carbon dioxide from decaying organic material.

The metamorphic limestones show much more variation than any other group; there is no apparent correlation between isotopic composition of these limestones and their physical and chemical properties, or their geographic or geologic distribution. Their isotope ratios are probably determined by the temperature of metamorphism and the amounts and isotopic compositions of the H_2O and CO_2 that passed through during recrystallization. For example, limestones recrystallized with very small amounts of water probably had little opportunity to change their original (sedimentary) isotopic composition, whereas those recrystallized in the presence of large amounts of ascending (magmatic) water and carbon dioxide might by exchange take on an isotopic composition similar to that of carbonatites. Such compositions were found, in fact, only in contact zones of igneous rocks.

Baertschi found, in the examples studied, that the abundance of heavy isotopes generally decreases with increasing distance from the contact zones. Metamorphic carbonates with the isotopic ratios of sedimentary limestones were found mainly in the central regions of large limestone bodies. The distances over which a considerable change in isotopic composition occurred ranged from a few centimeters to several meters.

Use of O^{16}/O^{18} as a Geologic Thermometer

Urey (1947) extended the calculations of Urey and Greiff (1935) and reported many new data on the abundance of isotopes. Here first appeared the suggestion of using the O^{18} content of $CaCO_3$ as a geologic thermometer. Urey calculated that a change in temperature of precipitation from 0° to 25°C should change the O^{18} content of $CaCO_3$ by a factor of 1.004. The limit of accuracy of mass spectrometers at that time made possible experimental determinations of paleotemperatures to about 6°C (for temperatures of formation below about 25°C). Urey pointed out that at higher temperatures the coefficient becomes smaller, but that it should be possible to get some indication of temperatures of formation considerably above 25°.

TABLE 28.—TEMPERATURE OF GROWTH OF BELEMNITES OF CRETACEOUS AGE
(Urey, 1948)

Zone	Specimen	T°C
Ostrea lunata	*Belemnita mucronata*	18.8
B. mucronata	*B. mucronata*	19.7
Actinocamax quadratus	*Actinocamax quadratus*	22.1
Offaster pilula	*Actinocamax* sp.	24.7
Marsupites testudinarius	*Actinocamax* sp.	26.5
Holaster subglobosus	*A. plenus*	17.5

Later, Urey (1948) described a mass spectrometric method for comparing two samples; it had an accuracy of 0.02% of the O^{18} content, which made possible determination of the temperature of formation to 1°C. To establish a temperature scale he measured the O^{18} content of modern shells and the temperatures of the waters in which they grew. The results plotted on a graph fall, for the most part, near a straight line with the calculated slope.

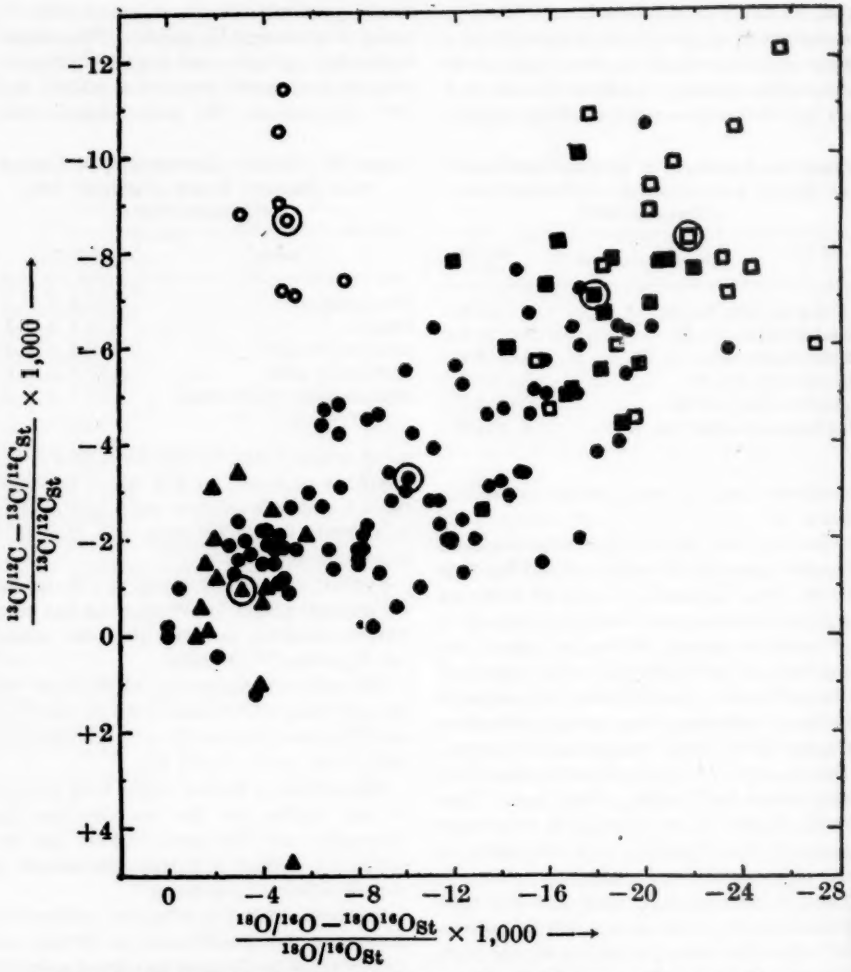
Urey emphasized that in determining unknowns it must be assumed that: (1) the isotopic content of ocean water was the same when the shell formed as it is now; (2) the organism did not fractionate the isotopes of oxygen significantly; (3) there has not been significant exchange since the $CaCO_3$ was formed.

He studied belemnites of Cretaceous age because they are massive and have had relatively little time to undergo exchange; also, because the ocean has probably not changed much isotopically since Cretaceous time.

The specimens studied were all from the Upper Cretaceous of Hampshire County, England (Table 28).

These results check geologic estimates of probable temperatures of seas of Cretaceous time.

McCrea (1950) calculated the variation in



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These results check geologic estimates of probable temperatures of seas of Cretaceous time.

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fractionation of the isotopes of oxygen in exchange reactions between dissolved carbonate and water and between precipitated calcite and water, and checked the results experimentally. He grew from solution calcite that gave the same isotopic composition of its oxygen as shells grown in the same water at the same temperature. A relation was obtained that gives the growth temperature in terms of O^{18} content

$$t = 18 - 5.44\,\Delta O^{18}$$

where t is in °C and Δ is expressed in per mil difference between O^{18} content of the unknown and of a standard gas. The constant 18 is characteristic of the standard gas used and must be changed if a reference gas of different isotopic composition is used. The constant −5.44 is the temperature coefficient and determines the slope of the curve; it is independent of the reference gas.

Urey, Lowenstam, Epstein, and McKinney (1951) made determinations of temperature of formation on 24 growth rings of a belemnite of Jurassic age 2.5 cm in diameter. The results show rhythmic fluctuations from about 15° to 20°C. The authors' interpretation is that the maxima represent summer temperatures, the minima, winter. If this interpretation is correct, then the diagram with its three maxima and three minima indicates that the animal lived between 3 and 4 years.

They also measured O^{18} and C^{13} contents of belemnites, brachiopods, oysters, and the enclosing 'chalk' from the Upper Cretaceous of England, Denmark, and the southeastern United States. The C^{13} contents of the limestones and their enclosed fossils did not agree within limits of measurement; O^{18} determinations agreed only roughly. The authors believe that the belemnites give the most reliable results because of their massive structure; the other shells and the enclosing limestone are more open and thus are probably subject to exchange.

The temperatures determined from the belemnites are as follows:

Upper Cretaceous of England, 14° to 24°C.
Upper Cretaceous of Denmark, 12° to 14°C.
Upper Cretaceous of southeastern U. S., 12° to 18°C.

Epstein, Buchsbaum, Lowenstam, and Urey (1951) extended Urey's 1948 work and developed a much more elaborate carbonate-water isotopic temperature scale. Their first three figures are graphs showing (1) salinity vs. O^{18} content for ocean waters, (2) same for surface ocean waters, and (3) temperature vs. O^{18} content for surface ocean water.

They determined O^{18} content of 13 samples of shells whose temperature of growth could be estimated accurately. A plot of temperature vs. O^{18} content (their Fig. 4) shows a marked trend, but the points by no means all lie on a line. The shells were heated 15 minutes, and O^{18} redetermined, after which all points fell on or very near a straight line. It is assumed that the shells contained variable amounts of some impurity which caused the original inconsistencies in the results, and which was driven out by the heating. The results from the heat-treated shells are taken as the currently best-available temperature scale. From them the following equation was derived

$$t = 14.8 - 5.41\,\Delta O^{18}$$

in which the terms have the same significance as in the equation already given from McCrea.

Neon and Argon

Suess (1949) calculates that some 10^7 times as much of (at least the lighter) rare gases have escaped as remain on the earth. There should, therefore, be a marked difference between the isotopic composition of these gases in the atmosphere and in stars, even though the terrestrial gases possessed the cosmic abundance of their respective isotopes when the earth was formed.

From the isotopic abundances of Ne and A in the atmosphere and the deduced equation showing the relation between abundance in the earth's atmosphere, cosmic abundance, and atomic weight of the gas, Suess calculates the cosmic abundance of the various isotopes of these gases (Table 29).

The values adopted by Bainbridge and Nier (1950) for atmospheric gases are as follows: Ne^{20}, 90.92; Ne^{21}, 0.28; Ne^{22}, 8.82; A^{36}, 0.337; A^{38}, 0.063; A^{40}, 99.60.

Suess concludes that isotopic analyses of Ne and A from meteorites, rocks, and natural gas

with much neon might "lead to a final decision on the correctness of the assumption suggested."

Lindemann and Aston (1919) first suggested fractionation of isotopes of atmospheric gases

TABLE 29.—ISOTOPIC COMPOSITION OF ATMOSPHERIC AND COSMIC NEON AND ARGON (Suess, 1949)

	Ne^{20}	Ne^{21}	Ne^{22}
Atmospheric Ne	90.51	0.28	9.21
Cosmic Ne (calc.)	93.4	0.2	6.4
	A^{36}	A^{38}	A^{40}
Atmospheric A	0.306	0.061	99.6
Same, without radiogenic A^{40}	83.0	16.5	~0.5
Cosmic A (calc.)	85.6	14.1	~0.4

under the influence of gravity. They calculated that at 100,000 feet the abundance of Ne^{22} should drop from 10% (the value accepted for near-surface neon at the time) to 8.15%; at 200,000 feet, to 6%. No one has yet studied the actual isotopic composition of neon from these altitudes.

SILICON

Jaeger and Dijkstra (1924) made very careful atomic-weight determinations of silicon from six terrestrial samples of sand, analcite, leucite, and chlorite, and from six stony meteorites with 30.8 to 41.0% SiO_2. No variations beyond experimental error were observed, so they concluded that there is no difference in the isotopic composition of terrestrial and meteoritic silicon. Their method, however, does not compare in accuracy with modern mass spectrometry.

Reynolds and Verhoogen (In press) have made a preliminary survey of the variations in the isotopic constitution of silicon from minerals and rocks. They report results for 14 samples (Table 30) in per mil excess Si^{30} over the value for a selected standard (olivine).

They point out that little, if any, fractionation of the isotopes of silicon would be expected in the straightforward crystallization of a silicate melt. Where aqueous or gaseous phases are present, however, fractionation would be expected, with the light isotope enriched in the gaseous phase. The geyserite of Yellowstone

TABLE 30.—ISOTOPIC COMPOSITION OF SILICON FROM VARIOUS SOURCES (Reynolds and Verhoogen, in press)

Material and Location	δ in ‰
Chert, Franciscan formation (Jurassic?), California	+1.0 ± 0.3
Marine diatomite (Miocene), Santa Barbara, California	+1.0 ± 0.4
Chert, Monterey formation (Miocene), Berkeley, California	+0.5 ± 0.2
Olivine, 90% Mg_2SiO_4, Jackson Co., North Carolina	0.0 —
Quartz from pegmatite, Topaz Lake, California	−0.1 ± 0.2
Oligoclase (An_{24}) from pegmatite, Topaz Lake, California	−0.4 ± 0.3
St. Peter sandstone (Ordovician), Beloit, Wisconsin	−0.4 ± 0.3
Augite from picrite basalt tuff, Mauna Kea, Hawaii	−0.7 ± 0.4
Stony meterorite, Melrose, New Mexico	−1.0 ± 0.3
Vein quartz, Hot Springs, Arkansas	−1.1 ± 0.2
Biotite from pegmatite, Topaz Lake, California	−1.5 ± 0.2
Diatomite, fresh water, California	−1.6 ± 0.2
Flint from Dover chalk, England	−1.8 ± 0.3
Geyserite, Yellowstone National Park	−2.1 ± 0.5

contains a larger percentage of the light isotope, Si^{28}, than any other material studied; it may have been brought up as silica dissolved in a compressed gaseous (aqueous) phase.

The small differences between the value for olivine and those for quartz and oligoclase of a pegmatite and the relatively large difference between the values for pegmatite and vein quartz suggest to the authors that these pegmatite minerals may have crystallized from a melt not too much below the temperature at which the olivine (dunite) crystallized, whereas the vein quartz was formed hydrothermally at a considerably lower temperature. The fact that biotite from the same pegmatite gives a value even lower than that for vein quartz

does not fit this concept. They suggest that the biotite formed from an aqueous phase, but in most pegmatites mica formed ahead of and along with the early quartz and feldspar. It should, therefore, according to the hypothesis of Reynolds and Berhoogen, give a value for δ between those of olivine and pegmatite quartz.

The difference between quartz and oligoclase in the pegmatite is in the same direction as the difference in oxygen ratios in quartz and potash feldspar in a pegmatite (Silverman, 1951, p. 34): the heavier isotope goes into the quartz preferentially.

The considerable difference between the ratios for olivine and a stony meteorite is puzzling. General considerations and findings on other elements in similar materials would lead one to predict closely similar ratios; Silverman found no significant difference in the ratio of oxygen isotopes in dunites and stony meteorites, and it is difficult to see how fractionation of silicon isotopes could occur without simultaneous fractionation of oxygen isotopes. Evidently, the problem needs more study.

Reynolds and Verhoogen observe an increase of Si^{30} with increasing percentage of secondary or precipitated silica, analogous to the increase in O^{18} found by Silverman. They prefer, however, to attribute it to organic processes rather than to exchange reactions, primarily because there is so little silica in sea water that it is difficult to see how such an exchange would take place. They suggest that enrichment of O^{18} in secondary silica may also be partly due to causes other than exchange with water.

Their results on the Dover flint (considerable enrichment in Si^{28}) contrast sharply with Silverman's finding of a considerable enrichment of O^{18} in the same material. No explanation of the discrepancy is offered.

They conclude that the small variations observed in the isotopic constitution of silicon presumably indicate a relatively simple geochemical history involving few opportunities for exchange with gas phases or aqueous solutions. The amount of separation cannot be accounted for simply by the value of the mass ratio 30/28 = 1.07, because this is practically the same as those for isotope pairs of sulfur, 34/32 = 1.06, and of carbon 13/12 = 1.08, for which much larger natural amounts of fractionation have been reported.

Sulfur

Thode and his coworkers have published several accounts of natural variations in the isotopic content of sulfur (Thode, Macnamara, and Collins, 1949; Macnamara and Thode, 1950; Szabo, Tudge, Macnamara, and Thode, 1950; Macnamara and Thode, 1951; Macnamara, Fleming, Szabo, and Thode, 1952). Bainbridge and Nier (1950) adopt a value of 22.7 for the ratio S^{32}/S^{34}. The average error in determining the ratio is given as ± 0.01. The results have been compiled from the five references given above (Table 31).

These relationships can best be visualized by means of a diagram showing the ranges of S^{32}/S^{34} for the various kinds of sulfur (Fig. 6).

A glance at the diagram shows that meteoritic sulfur has a very narrow range of values for S^{32}/S^{34} and that values for sulfur in terrestrial materials go significantly, and almost equally, above and below this range, and their average coincides approximately with the value for meteoritic sulfur. Sulfide ores of igneous origin appear to be enriched about 0.5% in S^{34} over the sulfur of igneous rocks, but too few specimens from too few localities have been studied to corroborate this. Macnamara and Thode (1950) take this to mean that, at the time the earth was formed, the isotopic content of its sulfur was the same as that now found for meteoritic sulfur, but that fractionation has occurred since. The ratios for sulfur of igneous rocks and for sulfide ores of igneous origin deviate only slightly from that of meteorites, but, as the materials move away from the igneous cycle, the deviations increase markedly.

Trofimov (1949) also studied the isotopic composition of meteoritic and terrestrial sulfur and found them to be the same (S^{32}/S^{34} = 21.93), except for the sulfate of sea water, which is enriched about 1% in S^{34}. This is in line with the results of Thode *et al.* Trofimov says that the results show that no isotopic fractionation takes place in interplanetary space. Both he and Macnamara and Thode remark that studies of other elements—Ga, Cu, Fe, and more recently oxygen—show no

TABLE 31.—ISOTOPIC COMPOSITION OF SULFUR FROM VARIOUS SOURCES (Thode and coworkers)

Materials	S^{33}/S^{34}
Meteorites:	
Siderite, Canyon Diablo, Arizona	22.21
Siderite, Canyon Diablo, Arizona	22.22
Siderite, Canyon Diablo, Arizona	22.21
Siderite, Canyon Diablo, Arizona	22.21
Siderite, Waterville, Washington	22.20
Siderite, Duchesne County, Utah	22.23
Siderite, Duchesne County, Utah	22.24
Siderite, El Toba, Argentina	22.22
Aerolite, Union County, New Mexico	22.20
Siderolite, Brenham, Kansas	22.23
Igneous rocks:	
Norite, Stillwater complex, Montana	22.08
Basalt, Parícutin Volcano, Mexico	22.13
Syenite, Otto Twp., Ontario	22.16
Norite, Murray mine, Sudbury, Ontario	22.17
Nipissing diabase, Helca mine, Cobalt, Ontario	22.18
Diabase, Ossion Twp., Ontario	22.21
Sulfide ores of igneous origin:	
Pyrrhotite, Falconbridge mine, Sudbury (1400′)	22.11
Pyrrhotite, Falconbridge mine, Sudbury (1700′)	22.08
Pyrrhotite, Falconbridge mine, Sudbury (2800′)	22.11
Pyrrhotite, McKim mine, Sudbury (1000′)	22.12
Pyrrhotite, Blezard Twp., Sudbury (1400′)	22.14
Pyrrhotite, Levack Twp., Sudbury (3000′)	22.10
Chalcopyrite, Levack Twp., Sudbury (3000′)	22.09
Pyrrhotite, Denison Twp., Sudbury	22.11
Pyrrhotite, Bowell, Foy offset, Sudbury	22.13
Phyrrhotite, massive sulfide, Sudbury	22.14
Pyrite, massive sulfide, Sudbury	22.10
Pyrite, massive sulfide, Falconbridge mine	22.13
Pyrite, Lamaque, Quebec	22.08
Pyrite, Lamaque, Quebec	22.12
Pyrrhotite, 40 miles NE. of Yellowknife, Northwest Territory	22.08
Chalcopyrite, calcite vein, Nu-Silco mine, Timiskaming, Ontario	22.12
Sulfide, hydrothermal vein in Nipissing diabase, Hecla mine, Cobalt, Ontario	22.14

TABLE 31.—*Continued*

Materials	S^{33}/S^{34}
Chalcopyrite, Stillwater complex, Montana	22.21
Pyrrhotite, Stillwater complex, Montana	22.17
Other pyrite samples:	
Pyrite, Dubuque, Iowa	22.465
Pyrite with calcite and fluorite, Tilly Foster mine, Brewster, New York	22.465
Pyrite with pyrrhotite, Kisbanya, Roumania	22.355
Pyrite in calcite, Rhode Island	22.345
Pyrite with scheelite, Mill City, Nevada	22.275
Pyrite with magnetite, Dognaska, Hungary	22.275
Pyrite, Echo Twp., Ontario	22.235
Pyrite, Tyrol, Austria	22.235
Pyrite in schist, Freiburg, Saxony	22.200
Pyrite with bornite, Magdalena, New Mexico	22.200
Pyrite, Madoc, Ontario	22.165
Pyrite with enargite, Cerro de Pasco, Peru	22.120
Pyrite, Park City, Utah	22.120
Pyrite, Milton, Vermont	22.120
Pyrite, Joplin, Missouri	22.070
Pyrite, Lanark County, Ontario	22.010
Pyrite, Gellivara, Sweden	22.010
Pyrite in chlorite, Chester, Vermont	22.000
Pyrite, Franklin, New Jersey	21.610
Samples of native sulfur:	
Native sulfur, Gulf of Mexico	22.370
Native sulfur, Gulf of Mexico	22.290
Native sulfur, Sicily	22.030
Native sulfur, Copper Cliff mine, Sudbury	22.230
Native sulfur, Mt. Vesuvius, Italy	21.81
Native sulfur, Italy	22.070
Native sulfur, locality unknown, I	22.41
Native sulfur, locality unknown, II	21.860
Native sulfur, lagoon in Cyrenaica, N. Africa	22.57
Native sulfur in well water, Dorchester, Ontario	22.705
Native sulfur in well water, Tillsonburg Ontario	22.285
Rock sulfates:	
Anhydrite Berchtesgaden, Bavaria	22.120
Gypsum, Caledonia, Ontario	22.035
Gypsum, Cayuga, Ontario	21.845
Gypsum, Parrsboro, Nova Scotia	22.015
Gypsum, Lockport, New York	21.690
Gypsum, Crystal Falls, Michigan	21.595
Gypsum, Mount Healy, Ontario	21.785

TABLE 31.—*Continued*

Materials	S^{32}/S^{34}
Sulfate in sea water:	
Halifax Harbor, Nova Scotia	21.70
Resolute Bay, Cornwallis Island (Atlantic)	21.73
Straits of Juan de Furca, Victoria, British Columbia	21.78
Pacific Naval Lab. No. 97 depth = 600 feet	21.80
H_2S from sulfur water:	
Port Ryersee, Ontario, 27 0-foot well	22.415
Port Stanley, Ontario, 300-foot well	22.215
Dorchester, Ontario	22.705
Dundas, Ontario, 150-foot well	22.610
Tillsonburg, Ontario	22.180
Organic sulfur:	
Commercial cystine (Eastman)	22.32
Human hair (Average of 6 runs 22.17 to 22.35)	22.25
H_2S from eggs	22.27
Coal	22.17
Petroleum	22.12
Miscellaneous:	
Sulfate in well water, Dorchester, Ontario	21.735
Sulfate in well water, Tillsonburg Ontario	21.715
Sulfate in well water, Port Ryersee, Ontario	21.650
Sulfate in well water, Port Stanley, Ontario	21.585
Sulfate in lagoon, Cyrenaica, North Africa	21.88
Pyrite with calcite and chalcopyrite, Gilman, Colorado	
Fine crystals	22.155
Coarse crystals	22.235
Sphalerite	21.89
Cinnabar	21.98
Galena	22.07

variation in isotopic ratios between terrestrial and meteoritic specimens.

Macnamara *et al.* (1952) point out that the sulfides of Sudbury are isotopically quite uniform and suggest that this fact may prove of great practical importance in determining the origin of the offset and marginal deposits of the district.

The temperature of formation of the pyrite samples studied by Thode *et al.* (1949, p. 369–370) was estimated by means of a "pyrite geothermometer", but there was little or no correlation between the temperatures thus determined and the isotopic ratios of the samples. Theoretical considerations indicate that there should be such a correlation for different specimens of the same mineral if they are formed by similar reactions. Excellent correlations have been demonstrated for other minerals and elements. Perhaps the pyrite geothermometer does not always give a close approximation to the true temperature of formation.

It is suggested that the very low ratio for pyrite from Franklin, N. J., may be due to high temperature of formation, or may mean that the iron was originally present as sulfate, which was later reduced to pyrite.

In two pyrite specimens with fine crystals inside and younger coarse crystals outside, the different kinds of crystals were analyzed separately. In both, the fine crystals showed a lower value for S^{32}/S^{34} (*see* Table 31), presumably because they were formed at higher temperatures.

Sulfate in sea water is enriched in S^{34} as compared to gypsum and anhydrite. Also sulfate in solution in well water is higher in S^{34} than either H_2S or free sulfur in the same wells. These relations might have been predicted from the reaction,

$$S^{34}O_2 + HS^{32}O_3^- \text{ (sol.)} \rightleftarrows S^{32}O_2 + HS^{34}O_3^- \text{ (sol.)} \quad K = 1.019$$

since sulfite is readily oxidized to sulfate. Moreover, Urey (1947, p. 572–574) has shown that the heavier isotopes of chlorine should, by chemical exchange, concentrate in compounds where chlorine shows higher valence states. By analogy, S^{34} would be expected to concentrate in sulfates with respect to S^{32}.

Hydrogen sulfide from shallow wells gave higher values for S^{32}/S^{34} than did samples from deep wells. The wells are in a natural-gas area, and presumably the H_2S came up from the gas-bearing strata. The change in the isotopic ratio is in the right direction to be explained by fractionation during diffusion.

Thode, Kleerekoper, and McElcheran (1951) reduced sulfate of known isotopic composition with anaerobic bacteria at 23–25°C. They found that:

$$\frac{S^{32}/S^{34}(H_2S)}{S^{32}/S^{34}(SO_4^-)} = 1.010 \text{ to } 1.012$$

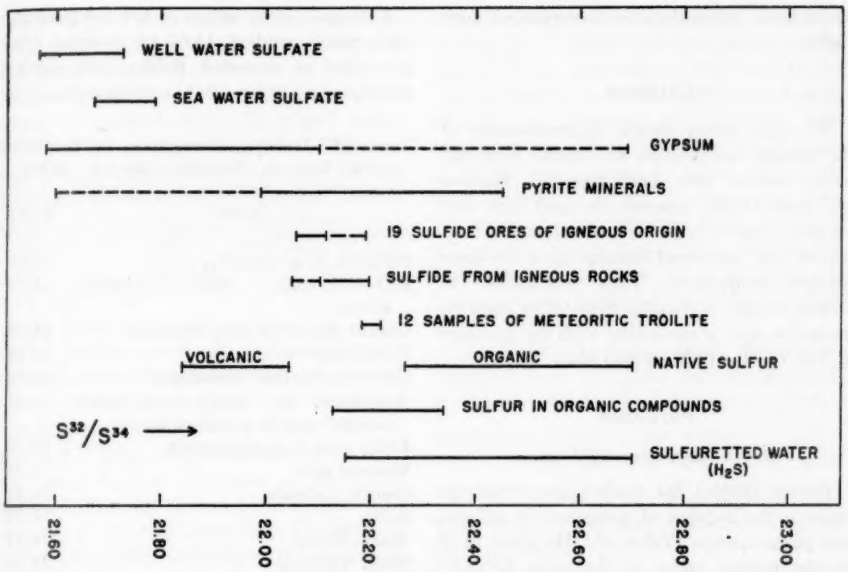

FIGURE 6.—CHART SHOWING RELATIVE ABUNDANCES OF S^{32} AND S^{34} IN SULFUR FROM VARIOUS SOURCES

which indicates that the H_2S is depleted in S^{34} by about 1%. This indicates fractionation in the direction, but not to the extent, that would be predicted from the equation:

$$S^{32}O_4^{=} + H_2S^{34} \leftrightarrows S^{34}O_4^{=} + H_2S^{32}; \quad K = 1.075(25°C.)$$

Macnamara and Thode (1951) report a larger fractionation (1.032) in the natural bacterial reduction of $SO_4^{=}$ to H_2S and subsequest oxidation to free sulfur in a lagoon in Cyrenaria, North Africa. They point out that native sulfur of organic origins is lower in S^{34} than is that of volcanic origin. On the basis of isotopic composition they venture the opinion that the sulfur of the Gulf Coast deposits in Texas and Louisiana ($S^{32}/S^{34} = 22.33 \pm 0.05$) was formed by the bacterial reduction of sea water sulfate and that the deposit near Gergenti, Sicily, ($S^{32}/S^{34} = 22.03 \pm 0.01$) is of volcanic origin.

Rankama (1952) has summarized these results on sulfur and presents a few new ones (Table 32) obtained by J. Noetzlin (La mesure des rapports isotopiques et ses applications possibles a la volcanologie. Manuscript to be published in Bull. Volcanol.).

TABLE 32.—ISOTOPIC COMPOSITION OF NATIVE SULFUR AND SULFUR FROM PYRITE (Noetzlin, quoted by Rankama, 1952)

Material	S^{32}/S^{34}
Native sulfur	
Volcanic	
Grande Soufriere Crater, Guadeloupe, West Indies	22.10 22.16 22.18
Naguisi Valley, Vanna Lava Island New Hebrides	22.30
Portes de l'Enfer, Pozzuoli, Italy	22.30
Sedimentary	
Sicily	21.89
Agrigento, Sicily	22.06
Pyrite	
Chizeuil, France	22.27

All of these values are well within the ranges reported for pyrite and for native sulfur by Thode and his co-workers. The relations between volcanic sulfur and that of organic origin (sedimentary) is here reversed, however. If the native sulfur from Sicily studied by Noetzlin

is of volcanic origin then the discrepancy is very slight.

Chlorine

No mass spectrometric determinations of the isotopic composition of chlorine from different sources have been reported. Harkins and Stone (1926), however, deduced from very accurate atomic-weight determinations that meteoritic and terrestrial chlorine have the same isotopic composition. They determined the atomic weight of chlorine from halite, apatite, wernerite, and a meteorite, with an accuracy of 3 to 7 in the fifth decimal place.

Potassium

K^{39}/K^{41} in Terrestrial Sources

Brewer (1936a) has studied the abundance ratio of the isotopes of potassium in mineral and plant sources (Table 33). He gives 14.25 as the normal value of the ratio K^{39}/K^{41}.[7] Minerals and potassium compounds from mineral sources deviate only slightly from this value.

Only two of the mineral sources studied show variations that may be significant; the vug crystal of calcite from wyomingite, which probably crystallized from water, is low in K^{41}; Hawaiian lava is slightly high. Brewer suggests that slightly greater solubility for K^{39} than for K^{41} will account for the observed differences. (It does not, however, account for the difference between lavas from Hawaii and those of Wyoming and Vesuvius.)

Much greater variations were observed in the K^{39}/K^{41} ratios of plant ashes, up to almost 15% in the concentrations of K^{41}. Of 32 results reported for plant ashes, 23 have ratios between 13.95 and 14.55 (0.3 below and above normal); several common trees and vegetables, rosin, tobacco, algae, and duckweed fall within this range. The only plant material showing a higher ratio (14.6) was potato sprouts 4 to 5 inches long. Potato pulp gives a normal value, so it appears that K^{39} migrates into the sprouts preferentially. A young potato vine gave a normal ratio, older ones were high in K^{41} ($R = 13.77$).

[7] Bainbridge and Nier (1950) adopt 13.48 ± 0.07 for this ratio.

Kelp gave lower values of K^{39}/K^{41} than any other plants studied, 13.67 for material dried and ashed as recovered. Boiling with distilled water and washing with hot water reduced the ratio to 12.63 and 13.37, respectively, indicating that K^{39} is preferentially removed.

Table 33.—Isotopic Composition of Potassium from Various Sources (Brewer, 1936a)

Material	K^{39}/K^{41}
Platinum (K as impurity)	14.24
$K_2O \cdot Al_2O_3 \cdot 2SiO_2$ (from commercial KNO_3)	14.32
Cement dust (from flue; 35% K_2O)	14.32
Searles Lake crude	14.25
Calcite crystal from wyomingite	14.60
Wyomingite (av. sample from several hundred pounds of crushed lava)	14.25
KNO_3 made from wyomingite	14.20
Vesuvius lava	14.27
Granite, Colorado	14.24
K_3PO_4	14.24
Basalt, Hawaii	14.11
Shale, Wyoming	14.23

That the abnormality of the ratio in kelp is not due to abnormal ratios in sea water is shown by a series of determinations on sea water. Brewer (1936b) determined K^{39}/K^{41} for 14 samples from various localities and from surface to depths of 2,500 m. Of these, ten gave 14.20; two, 14.21; one, 14.22; and one, 14.19. Error in measuring abundance was said to be in general <0.03% and rarely, if ever, >1.0%.

Brewer and Baudisch (1937) determined the K^{39}/K^{41} ratio for the mineral springs at Saratoga Springs, New York, and of the associated Cryptozoon reefs and the overlying shale and limestone. The spring water and Cryptozoon gave values of 13.85 ± 0.1 and 13.95 ± 0.1, respectively; the overlying shale and limestone 14.20 ± 0.03 and 14.00 ± 0.1. This is the only example reported of an inorganic source with a K^{41} content appreciably higher than normal. Physical mechanisms are probably precluded by the finding that the lithium in the water does not show a concentration of Li^7. The authors suggest that the simplest interpretation is "that the salt deposits from which the water arises are of marine plant origin rather than that any

isotope effect is occurring at the present time which would result in an abnormal abundance ratio for potassium" (p. 1579).

Later Brewer (1938a) republished some of the results on minerals and plants and added K^{39}/K^{41} ratios for clay from Puerto Rico and from North Carolina; both were 14.20. He also reported a number of results on animal tissues. All fell within the normal range except four samples of bone marrow, which were all high in K^{41}; human, 13.90; horse, 13.92; bull (old), 13.80; calf, 13.70.

Cook (1943) reviewed Brewer's work on the K^{39}/K^{41} ratio in nature and concluded that the observations should be supplemented by further studies. He determined the ratio for 37 samples of kelp, Cryptozoon, granite, basalt, diabase, mica, and feldspar, and found the average ratio in all of them to be the same as the normal value, 14.12, within 1% error. The rocks and minerals ranged in age from Early Precambrian to Tertiary. Many individual runs and some averages that were reported lie outside this range, but Cook explains these variations as isotope effects of the hot-filament ion source.

Cook then discusses where, in the light of artificial separation of isotopes, evidence might be found that a measurable isotopic separation has been effected in rocks. He concludes that, apart from biological processes, such processes as base exchange, replacement, etc. are likely to afford the best opportunity for natural separation of isotopes. He suggests that base exchange in zeolites and bentonite may offer the best natural example of such a process, but reports no experimental work on this or other geologic problems except the studies of potassium outlined above.

Bradt, Parham, and Brewer (1947, p. 104) conclude that the abundance ratio for the isotopes of potassium is constant (K^{39}/K^{41} = 14.20 ± 0.02) in nature, "except where base exchange or perhaps certain vital processes have taken place." No results on individual specimens are cited. Cook's 1943 paper is not mentioned.

Fractionation of Isotopes of Potassium (and Lithium) by Base Exchange with Zeolites

Taylor and Urey (1938) obtained a considerable isotopic fractionation of lithium and potassium by passing solutions of their salts through 30- to 35-foot columns packed with a sodium zeolite. The value of the ratio Li^7/Li^6 was increased by as much as 25% in the leading fraction and decreased by about the same amount in the tailing. For potassium the value of K^{39}/K^{41} was changed by about 10% in the same directions. Notice, however, that these two ratios are inverted with respect to weight of isotopes, which means that, whereas the heavier isotope of potassium is taken up and held preferentially, the lighter isotope of lithium is preferred by the zeolite.

The Hofmeister series shows the relative effectiveness of the alkali- and alkaline-earth elements in replacing one another from a zeolite:

$$Mg^{++} < Li^+ < Ca^{++} < Na^+ < Ba^{++} < NH_4^+ < K^+ < Rb^+ < Cs^+ < H^+$$

That is, lithium is the least strongly held, while cesium is the most strongly held of the alkali elements.

If the process is an equilibrium one, then the following equations are valid:

$$Li^{6+} + NaZ \rightleftarrows Li^6Z + Na^+$$
$$Li^{7+} + NaZ \rightleftarrows Li^7Z + Na^+$$

$$Li^{6+} + Li^7Z \rightleftarrows Li^{7+} + Li^6Z \qquad K = 1.022$$

similarly,

$$K^{39+} + K^{41}Z \rightleftarrows K^{41+} + K^{39}Z \qquad K < 1$$

and

$$N^{14}H_4^+ + N^{15}H_4Z \rightleftarrows N^{15}H_4^+ + N^{14}H_4Z \qquad K < 1$$

These results are for a specific set-up, and quantitatively they will be considerably modified by changes in temperature, rate of diffusion and reaction, kind of zeolite used, nature of solvent, etc. Some of these factors might even reverse the direction of the fractionation.

Brewer (1939a), with the results of Taylor and Urey in mind, set about to find whether base exchange has produced any considerable fractionation of the isotopes of potassium in nature. He measured K^{39}/K^{41} for 24 samples of various kinds of soil and phosphate rock, including clay, loam, diatomaceous earth, colloidal fractions, silt, greensand, fossil bones, and lava. They gave results remarkably uniform, 14.11 to 14.30, and near the normal value for this ratio. Brewer concludes that,

although base exchange is constantly taking place, the nearly constant potassium-isotope ratio indicates that mixing is likewise continuous.

K^{39}/K^{40} [8]

Suess (1939) and Schumb, Evans, and Leaders (1941) determined the relative abundance of K^{40} in terrestrial and meteoritic potassium. Both papers conclude that there is no difference that cannot be ascribed to experimental error (5 to 10%).

Brewer (1939b) found no differences for K^{39}/K^{40} for fresh Vesuvius lava, various clay soils, Saratoga Springs water, and commercial potassium salts.

Smythe (1939) obtained the same β-activity, within the probable error of 10%, for potassium from an old, deeply buried granite and from potassium salts from surface sources. The granite sample was from a mine in the Precambrian of Canada and had never been nearer the surface than 2500 feet. Smythe concludes that K^{40} is not formed by cosmic radiation at or near the earth's surface.

Iron

Valley and Anderson (1941) examined seven samples of terrestrial iron from different types of ore and widely separated localities and 12 samples from meteorites of various kinds. No localities are given in the note, nor are the details of results on individual samples recorded. They give the average isotopic composition for terrestrial and for meteoritic samples, and, for comparison, earlier results of De Gier and Zeeman (1935) and of Nier (1939a) (Table 34).

They conclude that the abundance of the stable isotopes of iron does not depend upon the place of origin of the specimen within the solar system, or the manner of its origin; in other words, that there has been no fractionation of the isotopes of iron by astronomic or geologic processes. They say that the differences between results on individual specimens are on the order of a few per cent and can be accounted for by instrumental effects. The values given by Valley and Anderson are adopted by Bainbridge and Nier (1950) for the isotopic composition of terrestrial iron.

Table 34.—Isotopic Composition of Terrestrial and Meteoritic Iron
(Valley and Anderson, 1941)

	Fe^{54}	Fe^{56}	Fe^{57}	Fe^{58}
Average of 7 terrestrial samples	6.37	100	2.37	0.34
Average of 12 meteoritic samples	6.32	100	2.32	0.33
De Gier and Zeeman (1935)	7.2	100	3.1	0.55
Nier (1939a)	6.6	100	2.3	0.31

Copper

Brown and Inghram (1947) measured the Cu^{63}/Cu^{65} ratio for two samples of terrestrial copper and one from the Canyon Diablo meteorite and obtained values of 2.236 and 2.234 for the former, 2.244 for the latter. They concluded that the difference (0.5%) is within experimental error, so there is no significant difference in isotopic composition of meteoritic and terrestrial copper.

Gallium

Inghram, Hess, Brown, and Goldberg (1947) found no significant difference in the Ga^{69}/Ga^{71} ratio of a sample of terrestrial gallium (1.510) and gallium from a meteorite (1.509). Sampson and Bleakney (1936),[9] however, obtained a value of 1.58, which is a much greater difference than experimental error. Inghram, Hess, Brown, and Goldberg suggest that the discrepancy may be due to voltage effects in the measurements of Sampson and Bleakney that were avoided in the later work. Sampson and Bleakney used gallium sesquioxide of unspecified source; Inghram and coworkers do not suggest that the difference might be real because the samples were from different sources.

Germanium

Graham *et al.* (1951) have made an exhaustive study of the isotopic constitution of germanium

[8] Bainbridge and Nier (1950) adopt a value of about 7,800 for K^{39}/K^{40}.

[9] In the original article there is a typographical error in giving Ga^{71} as the more abundant isotope.

from different occurrences. They measured both GeF_3^+ and $GeCl^+$ ions with the mass spectrometer; presumably the GeF_3^+ results are better since there is only one isotope of fluorine.

TABLE 35.—Ge^{70}/Ge^{76} RATIO OF GERMANIUM FROM VARIOUS SOURCES (Graham, *et al.*, 1951)

No.	Source of sample	Ge^{70}/Ge^{76}
1	Germanite from Tsumeb, South-West Africa	2.606 ± 0.005
2	Germanite from Tsumeb, South-West Africa	2.609 ± 0.006
3	Flue dust from coal mainly from County Durham, England	2.601 ± 0.003
4	Zinc ores of Joplin, Missouri	2.626 ± 0.003
5	Zinc concentrates from Picher, Oklahoma	2.608 ± 0.005

TABLE 36.—ISOTOPIC COMPOSITION OF GERMANIUM (Graham, *et al.*, 1951)

Isotope	Sample No. 4	All others	Bainbridge and Nier (1950)
Ge^{70}	20.45 ± 0.02	20.38 ± 0.02	20.55
Ge^{72}	7.41 ± 0.02	27.37 ± 0.02	27.37
Ge^{73}	7.77 ± 0.01	7.78 ± 0.01	7.61
Ge^{74}	36.58 ± 0.02	36.65 ± 0.02	36.74
Ge^{76}	7.79 ± 0.01	7.82 ± 0.01	7.67

They measured and reported the ratios of all the different isotopes; the pair Ge^{70}:Ge^{76} has the greatest mass difference and so should show a greater separation than any other pair of germanium isotopes. Only those results are recorded here, and only determinations made with GeF_3^+ (Table 35).

All the results except those on Sample No. 4 are within experimental error. No. 4 shows a difference of about 0.7% in the value of Ge^{70}/Ge^{76} from the average value for the other samples. In calculating the relative abundance of the various isotopes of germanium, therefore, the authors give out one set of values for Sample No. 4 and another for the others combined (Table 36).

When Sample No. 4 was purchased the supplier was not sure of its origin, but some months later supplied the information given in Table 36. In view of this uncertainty and of the fact that another sample from the Tri-State District agreed in isotopic composition with the rest of the samples, the authors did not attempt to interpret the difference shown by Sample No. 4.

BROMINE

Robinson and Briscoe (1925) recrystallized NH_4Br 2700 times in making a redetermination of the atomic weight of bromine and attempting to fractionate its isotopes. The atomic weight before and after the series of crystallizations differed by only 1 part in 40,000, from which Robinson and Briscoe concluded that fractional crystallization does not produce any separation of isotopes. This conclusion is not in accord with later results on the isotopic composition of rain water, snow, glacier ice, meltwater, etc. (*See* sections on Hydrogen and Oxygen.) Perhaps the percentage difference in the masses of the different isotopes of bromine is insufficient to allow their separation by this process, or possibly the recrystallizations were not performed under the proper conditions to effect a detectable separation. The mass ratio of the two isotopes, 81/79, is only 1.025, which is considerably lower than the ratio of any pair of isotopes for which significant natural fractionation has been reported.

RUBIDIUM

Brewer and Baudisch (1937) reported the Rb^{85}/Rb^{87} ratio to be about normal (2.6) for Saratoga Springs, New York, mineral water and associated Cryptozoon reefs, although they reported some fractionation of the isotopes of potassium in these materials.

Brewer (1938b) determined Rb^{85}/Rb^{87} for four lepidolites from California, zinnwaldite from Amelia, Virginia, and on rubber seed and apple seed, to be 2.61 ± 0.01. Artificial spodumene gave 2.59 ± 0.01. The value given by Bainbridge and Nier (1950) for this ratio is 2.591 ± .003.

URANIUM

Nier (1939b; 1939c) determined U^{238}/U^{235} from uraninite, curite, cyrtolite, cleveite,

dakeite, and Kolm, ranging in age from about 1×10^9 to 1.5×10^9 years. He obtained values from 137.5 to 141.3 but concluded that the differences were caused by the difficulty in maintaining a constant stream of vapor from the furnace. He believed, therefore, that there was no significant variation in the isotopic composition of any of the materials he used. He suggested a best value of 139.0 ± 1%, which is the one adopted by Bainbridge and Nier (1950).

Schumb, Evans, and Hastings (1939) obtained values of U^{235}/U^{238} for a granite and for the Pultusk meteorite that were almost twice as large as those obtained by Nier. They point out that the difference is only 1.5 times the probable error, and there is a 30 per cent chance that the true value differs from the observed by that factor. They conclude that the two sets of data are compatible and that no differences have been demonstrated in the isotopic composition of uranium either between terrestrial and meteoritic material, or between their terrestrial samples and Nier's.

PART II. TYPICAL CURRENT AND FUTURE PROBLEMS

Introduction

In the Introduction to Part I the writer stated that the time is right not only to summarize what has been done in the field of the geology of nonradiogenic isotopes, but also to point out other things that might profitable be done. In a discussion of assumptions and interpretations, several broad problems of the terrestrial, solar, and cosmic abundance of isotopes on which more data are needed were mentioned. Progress on most of these broad problems will be made only slowly; many data must accumulate for many years before significant advances can be made in answering most of those questions.

For other types of problems, however, a comparatively small amount of work can pay good dividends in new or better geologic interpretations. When the work already done has been brought together and summarized, it should not be difficult to see gaps in the information and to suggest researches that might help fill them. These can be new problems involving elements that have already been studied, or suggestions for work with pairs of isotopes of elements that have not yet been studied in this manner, where mass ratios, relative abundances, compounds involved, chemical properties, and other factors appear favorable.

There is no point in compiling a lengthy list of possible problems in isotope geology. Such inclusive and diffuse lists are likely to do more to confuse and stifle research in a given field than to sharpen and further it.

The following outline attempts to do three things:

(1) To mention the methods by which isotopes have been separated in the laboratory that probably have analogues in nature and to suggest the types of geologic situations in which each may have been operative.

(2) To suggest typical specific problems, which, on the basis of work already done, have a good chance of yielding positive results.

(3) To suggest pairs of isotopes which have not yet been investigated but which should, on theoretical grounds, be subject to measurable natural fractionation.

It will be convenient to combine at least (1) and (2) by giving specific problems as examples of things to look for under the various separation processes as they are outlined and discussed.

Physical Processes of Separation of Isotopes

Diffusion

A. *Diffusion of gases under low pressure.*—Studies of relative abundance and isotopic composition of elements in the earth's atmosphere and studies of the sun and some stars indicate that a considerable part of some of the lighter atoms and molecules have escaped from the earth by diffusion, and that the lighter isotopes have escaped preferentially. These things are to be expected on theoretical grounds and have been predicted for elements that have not been studied experimentally in this manner.

There is still much uncertainty as to how and when these losses took place. If the earth was once molten, they would have taken place largely at that time, with relatively little escape after the condensation of the oceans and the earliest formation of sedimentary rocks. If the earth was formed by accretion, however, time and amount of escape would depend on the magnitude of the gravitational field, amount of atmosphere, and the temperature of the surface and/or upper atmosphere (exosphere) at a given time.

Geologic studies have produced no positive evidence on this point. Vernadsky, Vinogradov, and Teis (1941) determined the water driven from old crystalline schists to be heavier than that from younger minerals and rocks and much heavier than modern surface water. This could indicate continued escape of H^1 or the lighter water molecules, or both. Isotopic analysis of two of the samples showed that the increased density was due to more O^{18} rather than increased H^2. One would expect H^1 to escape much more rapidly with respect to H^2 than O^{16} with respect to O^{18}, or H_2O^{16} with respect to H_2O^{18}.

The interpretation of preferential escape, therefore, is very tenuous, and much more

work is needed. The abundance and isotopic composition of H_2, H_2O, N_2, and Ne for many minerals with the greatest possible range of geologic age should be determined accurately to see whether any relation between age and isotopic composition can be demonstrated.

If these differences are sufficiently great for H_2O, it may be possible to establish a time scale for sedimentary rocks by determining the isotopic composition of connate water in series of rocks, from Precambrian to present, laid down in similar environments at about the same temperatures (or correcting for temperature).

If, during geologic time, diffusion out of the earth's field of gravitation has removed a significant part of the lighter molecules of water and its components from the atmosphere and the surface of the earth, then we should expect heavier water not only in old hydrous minerals, but also in juvenile water in volcanic emanations, fumaroles, and hot springs.

If it could be established, for example, that magmatic water has certain O^{16}/O^{18} and H^1/H^2 values (or characteristic ranges of values) different from those of ground water, then, by determining the isotopic composition of water from hot springs and of uncontaminated ground water from the same area, it should be possible to estimate the proportion of magmatic water in a given hot spring or geyser, or in volcanic gases.

Since the gases from even a very active volcano are contaminated by admixtures of atmosphere and ground water, it would be necessary to obtain water that was fixed by magmatic processes *at depth* and that has not been free to move or change its isotopic composition since. Such water might be found in the primary hydrous minerals of deeply eroded batholiths. For example, hornblende from the fresh granodiorite of the Sierra Nevada batholith, say at the bottom of Yosemite Valley, might provide a good sample of original water. Samples from several different and widely separated locations should be studied in any attempt to determine the isotopic composition of telluric water.

Water from Mammoth Hot Springs in Yellowstone National Park is 21 ppm heavier than the ground water of that region, and it is estimated that the springs contain 10% of juvenile water. When a value is available for juvenile water from deep-seated rocks, the value from Mammoth Hot Springs should be extrapolated to 100% juvenile water and compared with the value for water from deep-seated rocks.

Such determinations might shed some light on the problem of the origin of the oceans. If they were condensed from a primitive atmosphere and have had only minor additions, the isotopic composition should differ from that expected if they have been accumulating throughout geologic time as the water is expelled from crystallizing magma.

Similar studies and interpretations might also be made by studying the isotopic composition of juvenile CO_2 and comparing it with CO_2 from other sources.

B. *Diffusion of gases and percolation of liquids through porous media under moderate pressure.*—In geologic phenomena, it is not always possible to separate these two cases with certainty. Gaseous diffusion even at 1 atmosphere pressure is a very inefficient method of separating isotopes in the laboratory. If the column is long enough, however, and if motion is always in one direction so that remixing is prevented, significant separation might be effected in nature even at considerably higher pressures.

1. VOLCANIC GASES: For example, if H_2, CO_2, SO_2, HCl, NH_4Cl, and other components of volcanic gases have moved far through volcanic rock and other material in coming to a vent, they may have undergone enough isotopic fractionation so that interpretations of distance and velocity of migration, etc., might be attempted. It would have to be possible to evaluate independently other factors that might affect the isotopic compositions, such as the effect of temperature, original composition, equilibrium between different compounds containing the same element(s), etc.

2. GRANITIZATION: Studies of the distribution of nonradiogenic isotopes in granite masses may give positive information on the problem of granitization vs. magmatic granite. Quite different isotopic patterns would be expected from the two processes.

In a crystallizing mass the heavier isotopes of elements like Si, Mg, and Ca would be expected in the outer zone of the intrusion in the first minerals to crystallize, whereas in a mass of similar composition formed by diffusion, permeation, and migration of ions, the

lighter isotopes would be expected to move farther and therefore would be found near the borders of the body. The situation with water, however, might be expected to be reversed. Anderson *et al.* (1937, p. 1499–1500) and Vernadsky, Vinogradov, and Teis (1941, p. 574) demonstrated that artificial salts and minerals hold the lighter water molecules more tenaciously than they do the heavier ones. Conversely, we should expect the light water molecules to be taken up first—*i.e.*, at a higher temperature—which would tend to enrich the periphery of a magmatic granite in lighter molecules of water, whereas the heavier ones would collect near the center of a granitized mass.

3. ORE-FORMING SOLUTIONS: Relations similar to those postulated for granitized areas would be expected for veins formed by percolating hydrothermal solutions. If the assumptions are correct, then determinations of isotopic composition along the strike and down dip of the vein should make possible determination of the direction from which the solutions came. This assumes that temperature of formation can be estimated independently from liquid inclusions, or by some other means.

4. MIGRATION OF ATOMS OR IONS THROUGH CRYSTAL LATTICES IN SOLID ROCKS (METAMORPHIC DIFFERENTIATION): If this process, envisioned by some Scandanavian geologists, is operative at all, it should produce a relatively high degree of isotopic separation per unit distance. In the formation of the leptites of Finland, for example, if silicon atoms have migrated into the silica-rich layers, and iron, calcium, and magnesium, for example, have moved into the other layers,[10] then the silicon in the silica-rich layers should have more Si^{28} and the iron, magnesium, and calcium in the other layers should have more of the lighter isotopes (higher values of Mg^{24}/Mg^{26} and Ca^{42}/Ca^{43}).

Eskola (1950) and Tuominen and Mikkola (1950) present two other points of view on the supposed magnesium metasomatism of the Fennoscandian shield.

5. GASEOUS EMANATIONS FROM PETROLEUM DEPOSITS: Helium, methane, hydrogen sulfide, and other gaseous emanations from petroleum deposits might be expected to undergo detectable isotopic fractionation as they move out through the slightly permeable overlying materials. Helium should show the greatest separation because the percentage difference in weight between He^3 and He^4 is greater than between any expectable molecules that might be involved. Helium, however, is by no means universally associated with petroleum deposits; moreover, He^4 at and near the earth's surface is probably mostly radiogenic, and He^3 is probably the product of bombardment by cosmic-ray neutrons.

Even with these complications a more or less systematic variation in the He^4/He^3 ratio might be detectable around a given petroleum deposit, or type of deposit. He^3 should move out more rapidly and thus be relatively more abundant farther from the source. However, He^3 is much more abundant in atmospheric than in oil-well helium, so contamination with atmospheric gases might partly or completely mask the expected effect.

Other gases, therefore, such as CH_4 and H_2S, may be more generally useful in this type of exploration. For example, in water wells in and near Canadian oil fields, the sulfur of the H_2S has a higher S^{32}/S^{34} ratio in the shallower wells (Thode *et al.*, 1949, p. 371–372), which would be expected if the H_2S has come from underlying petroliferous strata and has undergone some isotopic fractionation as it moves up and out. Methane should show a similar effect; a sufficiently detailed and careful study might demonstrate a new technique of prospecting for oil in this fractionation effect.

For example, plotting *isorats*[11] of S^{32}/S^{34} in H_2S or of C^{12}/C^{13} for methane over a large area might localize the structure from which the gas is escaping. With sufficient experience it might even be possible to estimate the distance to the structure from the value of a given ratio.

6. FLOW OF GROUND WATER THROUGH AQUIFERS OVER GREAT DISTANCES: It might be

[10] Barth (1952, p. 313) states that in such a process the oxygen framework would be essentially fixed and the "wandering interstitial metals" would migrate through it. If this is the case, then the O^{16}/O^{18} ratio should be the same in all the layers.

[11] A term here proposed for lines connecting points having *equal ratios* of two or more elements or of two or more isotopes of the same element. In general, isorats of isotopes should not be plotted for rock or soil samples, but only for a given compound, or type of compound. For example, an isorat for S^{32}/S^{34} might be plotted using different sulfides at different points, where the same sulfide does not occur at all points studied, but would not be plotted for sulfides at some points and sulfates at others.

expected that in an aquifer with fine pores the lighter molecules of water would move enough more rapidly than the heavier ones that measurable fractionation would be produced if the water traverses sufficient distances. If such a fractionation is produced, then measurements of it could help in solving problems of distances and direction of flow.

If the water has been out of contact with the air since leaving the intake area and if it has been in the aquifer long enough, then its age can be determined by the C^{14} method, and the average velocity of the water over long distances could be determined. W. F. Libby (Personal communication) has recently found that H^3 is concentrated in rain, under certain conditions, up to twenty-fold or more over its concentration in normal river water. High concentrations are especially likely in semiarid regions where rains are infrequent and there is time between them for accumulation in the atmosphere of H^3 produced by cosmic-ray activity. Outcrops of aquifers on the High Plains, therefore, might be expected to receive rainfall considerably enriched in H^3. The half-life of this isotope is about 12 years, so if the motion of the water through an aquifer is too rapid for study by means of C^{14} determinations (half-life = ca. 5600 years) then H^3 might be used.

However, it is by no means certain that the lighter molecules of water will move through an aquifer more rapidly than heavy ones. There is evidence that minerals such as clays and zeolites may take and hold the lighter molecules preferentially (Anderson *et al.*, 1937, p. 1499–1500; Vernadsky, Vinogradov, and Teis, 1941, p. 574), in which case the two opposing processes would have to be evaluated experimentally. (*See* section on Base Exchange.)

C. *Diffusion through a thermal gradient.*—It is difficult to evaluate diffusion through a thermal gradient as a natural method of isotopic fractionation. There are probably no natural situations closely parallel to the hot-wire or hot-cylinder techniques that are so effective in separating isotopes in the laboratory. A less efficient separation of mass constituents occurs when a gas mixture diffuses freely in a vessel whose ends are at different temperatures. Enskog (1911) and Chapman (1917, p. 192–196) demonstrated independently that under these conditions the heavy constituent is more abundant at the cold end. This situation may find analogies in the sharp thermal gradients at and near the contacts of batholiths, stocks, dikes, veins, etc.

If the analogy holds, then the heavier isotopes would tend to migrate into the cooler wall rock. This tendency is opposed to the effect of isothermal diffusion through a porous medium, in which the lighter isotopes would tend to move out from the source more rapidly. Add to these factors the isotopic fractionation produced by chemical-exchange equilibria (discussed below), which changes in amount with temperature, and the situation in contact zones becomes very complicated indeed. If paleotemperatures across contacts can be estimated independently, then it may be possible to evaluate the other two effects relatively by detailed studies of isotopic compositions of the same compounds across such contacts.

If these evaluations can be made, then isotope studies may be helpful not only in determining paleotemperatures, but also in problems of motion of solutions, distances to which thermal effects extend, etc.

D. *Diffusion under the influence of gravity.*—Since the atoms of two isotopes of an element differ appreciably in mass, but not in size, it is expectable that in a system at equilibrium under the influence of gravity alone there will be an appreciable separation of the isotopes, with the heavier one collecting in the lower part of the system. In nature, however, disturbing factors such as convection currents, adverse diffusion, and adsorption are commonly operative so that the separation is less than the theoretical if, indeed, it can be demonstrated at all.

1. IN THE ATMOSPHERE: Lindemann and Aston (1919, p. 530–532) have calculated the expected variation in neon isotopes at great height in the atmosphere. Taking the Ne^{22} content of neon at ground level as 10% (Bainbridge and Nier, 1950, adopt a value of 8.82 ± 0.04), they calculated that at 100,000 feet the Ne^{22} content should be 8.15%; at 200,000 feet it would be 6%.

Nitrogen is the only gas for which gravitative isotopic fractionation has actually been measured. Chackett, Paneth, Reasbeck, and Wiborg (1951) detected relative enrichment of the atmosphere in He and Ne and impoverishment in

A at heights of about 65–72 km, although previously no changes had been found up to about 66 km. Isotopic fractionation was not demonstrated; even if it cannot be shown to be effective at 70 km. it will almost certainly be measurable, at least for lighter elements and compounds, at greater heights.

These studies should be continued and extended to still greater heights, where measured isotopic fractionation of N_2, H_2, H_2O, Ne, etc., can be compared with the amount predicted on theoretical grounds. These studies will no doubt provide additional information about currents in the atmosphere at great heights and the mechanism of movement of material from the surface of the earth to those heights.

When samples from still greater heights are available, another approach should be possible. If the theory is correct that C^{14}, He^3, and perhaps other isotopes are produced much more rapidly in the ionosphere than near the surface of the earth, then samples of the atmosphere from that zone should show relatively more of these isotopes than would be expected on the basis of gravitational fractionation. Study of samples from various places in the ionosphere should indicate the height of maximum effect and whether it is the same for all elements. Study of the abundance of these isotopes from the level of maximum production to ground level should provide information about the mechanism and rate of exchange of material between the ionosphere and stratosphere, and between the stratosphere and the troposphere.

Samples from even greater altitudes might help to answer a more fundamental question, or at least one that is of more interest geologically, "Are gases still escaping from the earth's gravitational field at a rate that can be detected?"

There is little doubt that isotopic fractionation will be demonstrated for at least all the lighter atmospheric gases when samples are available from sufficient height. But if gases are now escaping from the upper atmosphere then samples from extreme heights should show a reversal of the trend—*i.e.*, the heavier isotopes should increase in relative abundance at those heights because of more rapid escape of the lighter ones. This study should be made for helium and hydrogen first; if preferential escape of the lighter isotopes can be demonstrated for these elements, then H_2O, Ne, N_2, O_2 and progressively heavier particles should be investigated until an upper weight limit for the effect is demonstrated.

G. P. Kuiper (Personal communication) suggests that measurements of He/A ratios will be better for this purpose than any pair of isotopes of a single element. He doubts, however, that any reversal of fractionation with height will be observable.

Recent calculations by Spitzer (1951, p. 243) indicate that only hydrogen and helium are escaping at a rate that would have produced a significant effect during geologic time. Kuiper (1951, p. 311 ff.) and Urey (1952a, p. 99–100; 142–149) also discuss the problem of escape of gases from the atmosphere; all three give numerous references to earlier works, many of which contain calculations of rate and time of escape. Some of the results, not much less recent than Spitzer's, give times of escape less than his by a factor of about 10^6. The differences are due primarily to differences in assumptions that at present are not subject to experimental testing. The technique suggested above, therefore, will be worth while if it can demonstrate the reality of escape and give any kind of comparison of rates of escape of particles of different masses.

2. IN THE HYDROSPHERE: As mentioned in the section on Hydrogen, some studies have indicated increased density of water at depth in lakes and seas, such as Lake Baikal and the Black Sea. Later work has not substantiated some of the examples, but too few determinations have been made to prove whether such differences exist. Many more measurements should be made, not only from deep lakes and closed seas, but also from extreme depths in the open ocean, especially from the bottoms of long, deep trenches like the Mindanao Deep where there may have been no disturbing currents.

Studies should be made not only of the isotopic composition of the water, but also of some of its dissolved material, particularly Li, Mg, Cl, and Ca. If systematic increases of the heavy isotopes of any of these components can be demonstrated at great depth in quiet water, then isotopic studies may suggest, or confirm, deposition of certain types of sediments in similar environments.

The determinations should be made, of course, on connate water, its dissolved material, or components precipitated from it *at depth*, rather than on clastic particles or precipitates that formed nearer the surface and settled into the deep basin. However, since it is so very difficult to be sure that contained water is connate it may turn out instead that such studies will have to be used as an aid in demonstrating the presence of connate water in sedimentary rocks.

3. IN THE LITHOSPHERE: There is little chance that isotopic fractionation can be brought about in the crust of the earth by gravity. It is not beyond the realm of possibility, however, that gravity may have had some effect in that direction during the crystallization of large masses of rock.

Suppose, for example, that olivine is crystallizing slowly from the magma in a large reservoir and settling to the bottom to form dunite. Two factors would favor accumulation low in the mass of crystals containing heavier isotopes: (1) heavier isotopes would tend to combine at higher temperatures and thus to form crystals slightly earlier than the lighter isotopes and (2) crystals composed of heavier isotopes would have a higher density and would sink through the magma more rapidly. The first factor would be favored by very slow cooling and crystallization, because the atoms of higher mass could seek each other out and so form crystals relatively rich in the heavier isotopes before a temperature is reached at which crystals containing only the lighter isotopes are stable.

This is an idealized picture, of course, and we should not expect to find any crystal composed entirely of heavy or light isotopes, but with very slow crystallization of a large mass there might be a detectable concentration of heavy isotopes in the early crystals that accumulate along the floor.

If crystal flotation is operative in crystallization differentiation (1) and (2) work in opposite directions, and it would have to be determined experimentally whether one or the other dominates, or whether they essentially cancel each other.

For olivine, determinations of O^{16}/O^{18}, Mg^{24}/Mg^{26}, Si^{28}/Si^{30}, and Fe^{54}/Fe^{56} should all be made on samples from bottom to top of the dunite mass. For plagioclase (crystal flotation) O^{16}/O^{18}, Si^{28}/Si^{30}, and Ca^{42}/Ca^{48} should be determined for all the feldspar-rich layers.

Evaporation

It has been demonstrated repeatedly and conclusively that sea water contains enough D and O^{18} to make it about 1.5 ppm heavier than fresh surface water. Water from the Dead Sea, which has been subjected to a great deal more concentration by evaporation than has ocean water, when compared with fresh water, shows about twice as much difference in density (about 3 ppm).

Playas that have been repeatedly evaporated, almost but never completely to dryness, might contain water of still greater density. Also, the solutions from which deposits of evaporites formed may have contained a higher proportion of heavy water than less-concentrated bodies of water. If this concentration of heavy isotopes is continuous, interesting possibilities emerge.

For example, controlled isotopic studies (comparison with isotopic distributions obtaining during artificial evaporation of sea water) might make it possible to estimate the stage of evaporation and crystallization reached when a given crystal or layer of crystals formed, especially in a relatively undisturbed sequence. It might be possible to distinguish primary and secondary (recrystallized) or otherwise disturbed parts of a bed or deposit in this manner, or to determine the place in a sequence where there was influx of fresh water or a new flow of unsaturated sea water into the crystallizing basin.

Each of these problems will, of course, require much supporting research before any firm interpretations can be made. In problems of evaporation of salines, for example, at least the following questions would need to be answered by experimental work on evaporation of sea water:

How much enrichment in O^{18} and H^2 is produced in a single cycle? Are evaporites produced in a single cycle? If not, what effect will additional cycles have on isotopic composition of the water? How is the enrichment affected by rate of evaporation? Temperature at which the evaporation takes place? Pressure? Nature of the solution? Concentration of the solution?

There is a difference of opinion as to how

the ulexite nodules and lenses in some of the South American borate deposits formed—whether they are true evaporites or were formed in playa deposits by percolating ground water. The distinction is important; if they were formed by the latter process, they would occur over a much larger area than if they were formed only where water covered the floor of the basin.

If these deposits precipitated from concentrated playa waters, their contained water would almost certainly be significantly heavier than if they were formed by percolating ground water that had had little or no opportunity for isotopic fractionation. By comparison of the water with that of similar borates known to be evaporites, and with water of the same borates precipitated from fresh water, a good indication of the origin might be obtained.

Sublimation

It is generally agreed that wastage of glaciers, ice sheets, and snow by differential melting and sublimation produces isotopic fractionation, but the magnitude and even the direction of that fractionation have by no means been firmly established.

Detailed studies on individual glaciers, or types of glaciers, however, should establish fractionation patterns that might allow relative dating of ice layers in a given glacier, or in different glaciers that have been wasting under similar conditions of temperature, atmospheric pressure, relative humidity, and comparative access of different layers to the open atmosphere.

If methods for absolute dating are at hand, such as C^{14} determinations on organic material in some of the layers, then isotope determinations of H_2 and O_2 on layers that do not contain organic material may enable an estimate of absolute age[12].

Chemical Processes of Separation of Isotopes

Exchange Reactions

In 1935 Urey and Greiff discussed thoroughly the method of treating isotopic exchange equilibria theoretically. Previously, Urey and Rittenberg (1933), Rittenberg and Urey (1934a; 1934b), and Rittenberg, Bleakney, and Urey (1934) had calculated the equilibrium constants of simple reactions involving the lighter isotopes of hydrogen and had confirmed the results experimentally.

Urey and Grieff consider equilibria of the type

$$O_2^{16} + 2H_2O^{18} \rightleftarrows O_2^{18} + 2H_2O^{16}$$

for which

$$K = \frac{f(O_2^{18})}{f(O_2^{16})} \times \frac{f^2(H_2O^{16})}{f^2(H_2O^{18})}$$

where f is the distribution function of the respective molecules. The equilibrium constant, K, depends upon the ratios of the distribution functions of like isotopic molecules. Urey and Greiff calculated and tabulated the equilibrium constants and enrichment factors (α)[13] at 273.1°, 298.1°, and 600°A, (0°, 25°, and 327°C) for $O^{16}:O^{18}$, $C^{12}:C^{13}$, $Cl^{35}:Cl^{37}$, $Br^{79}:Br^{81}$, $Li^6:Li^7$, and $N^{14}:N^{15}$ in 24 simple equations of the type mentioned above.

Urey (1947, p. 575) added several equations taken from the literature involving some of the pairs of isotopes mentioned above and others involving $S^{32}:S^{34}$; $S^{32}:S^{36}$; H^1H^2; and H^1H^3. Although not many of these reactions have been used in geologic interpretations most of them can be so used, and it will be convenient to have all those of geologic interest listed together (Table 37).

Most of the values given for K and α in Table 37 are calculated ones, but enough of them have been checked experimentally to prove that the theory is sound, and that the theoretical values are very close to those determined experimentally. Several have already been used in geologic interpretations of considerable importance. For example, Urey and his coworkers (1948; 1951) have used equation (5) to determine temperatures of formation of limestone, shells, and other forms of $CaCO_3$. Equation (10) predicts that the oxygen of the atmosphere is higher in O^{18} than is the oxygen of ordinary water, and explains why. Numbers

[12] Irving Friedman, of the U. S. Geological Survey, is making a study of this kind of the Grasshopper Glacier in Montana.

[13] The enrichment factor, α, is $\frac{N_1}{N_2} \Big/ \frac{n_1}{n_2}$ where N_1 and N_2 are the numbers of light and heavy atoms in the one compound and n_1 and n_2 the corresponding numbers for the other compound.

TABLE 37.—ISOTOPIC EXCHANGE EQUILIBRIA

No.	Reaction	Equilibrium Constants (K)			Enrichment Factors (α)		
		0°C	25°C	327°C	0°C	25°C	327°C
1	$SO_2^{35} + 2H_2O^{18}(g) \leftrightarrows SO_2^{18} + 2H_2O^{16}(g)$	1.069	1.057	1.005	1.034	1.028	1.003
2	$SO_2^{35} + 2H_2O^{18}(l) \leftrightarrows SO_2^{18} + 2H_2O^{16}(l)$	1.040	1.028		1.020	1.014	
3	$CO_2^{16} + 2H_2O^{18}(g) \leftrightarrows CO_2^{18} + 2H_2O^{16}(g)$	1.128	1.110	1.028	1.064	1.054	1.014
4	$CO_2^{16} + 2H_2O^{18}(l) \leftrightarrows CO_2^{18} + 2H_2O^{16}(l)$	1.097	1.080		1.047	1.039	
5	$CO_3^{16-}(aq.) + 3\ H^3O^{18}(l) \leftrightarrows CO_3^{18-}(aq.) + 3H_2O^{16}(l)$				1.033	(1.036, exp., 0°C)	
6	$SO_4^{16-} + 4H_2O^{18}(g) \leftrightarrows SO_4^{18-} + 4H_2O^{16}(g)$	1.156	1.123	1.004	1.037	1.029	1.001
7	$SO_4^{16-} + 4H_2O^{18}{}_4(l) \leftrightarrows SO_4^{18-} + 4H_2O^{16}(l)$	1.093	1.062		1.028	1.015	
8	$CO^{16} + H_2O^{18}(g) \leftrightarrows CO^{18} + H_2O^{16}(g)$	1.048	1.042	1.014	1.048	1.042	1.014
9	$CO^{16} + H_2O^{18}(l) \leftrightarrows CO^{18} + H_2O^{16}(l)$	1.033	1.028		1.033	1.028	
10	$O_2^{16} + 2H_2O^{18}(g) \leftrightarrows O_2^{18} + 2H_2O^{16}(g)$	1.048	1.041	1.005	1.024	1.020	1.003
11	$O_2^{16} + 2H_2O^{18}(l) \leftrightarrows O_2^{18} + 2H_2O^{16}(l)$	1.020	1.012		1.010	1.006	
12	$SO_2^{16} + O^{18} \leftrightarrows SO_2^{18} + O_2^{16}$	1.020	1.015	0.9998	1.010	1.008	1.000
13	$2CO^{16} + O_2^{18} \leftrightarrows 2CO^{18} + O_2^{16}$	1.047	1.044	1.023	1.023	1.022	1.011
14	$SO_4^{16-} + 2O_2^{18} \leftrightarrows SO_4^{18-} + 2O_2^{16}$	1.051	1.036	0.993	1.013	1.009	0.998
15	$CO_2^{16} + CO_2^{18} \leftrightarrows 2CO^{16}O^{18}$	3.9990	3.9993	4.0000	0.9997	0.9998	1.000
16	$C^{13}O + C^{12}O_2 \leftrightarrows C^{12}O + C^{13}O_2$	1.098	1.086	1.029	1.098	1.086	1.029
17	$C^{13}O_3^- + C^{12}O_3^- \rightleftarrows C^{12}O_2 + C^{13}O_3^-$	1.015	1.012	0.997	1.015	1.012	0.997
18	$HC^{13}O_3^- + C^{12}O_2 \leftrightarrows HC^{12}O_3^- + C^{13}O_2$				(Exp. > 1.014, 25°C)		
19	$C^{13} + C^{13}O \leftrightarrows C^{12} + C^{13}O$		1.074	1.030		1.074	1.030
20	$C^{13} + C^{13}O_2 \leftrightarrows C^{12} + C^{13}O_2$		0.989	1.002		0.989	1.002
21	$Cl_2^{35} + 2HCl^{37} \leftrightarrows Cl_2^{37} + 2HCl^{35}$	1.007	1.006	1.0003	1.004	1.003	1.00015
22	$Br_2^{79} + 2HBr^{81} \leftrightarrows Br_2^{81} + 2HBr^{79}$	1.001	1.0008	0.99994	1.0005	1.0004	0.99997
23	$Li^6H + Li^7 \leftrightarrows Li^7H + Li^6$	1.028	1.025	1.008	1.028	1.025	1.008
24	$Li^7Z + Li^6 \leftrightarrows Li^6Z + Li^7$				(Exp. 1.022, 22°C)		
25	$Li^7(amal.) + Li^6Cl \leftrightarrows Li^6(amal.) + Li^7Cl$				(Exp. 1.025 22°C)		
26	$N_2^{14} + 2N^{15}O \leftrightarrows N_2^{15} + 2N^{14}O$	1.033	1.030	1.015	1.016	1.015	1.007
27	$N^{15}H_3 + N^{14}H_4^+ + \leftrightarrows N^{14}H_3 + N^{15}H_4^+$				(Exp. 1.034, 25°C)		
28	$N^{15}H_3 + N^{14}H_3\ (aq.) \leftrightarrows N^{14}H_3 + N^{15}H_3\ (aq.)$				(Exp. 1.006, 25°C)		
29	$S^{34}O_2 + HS^{32}O_3^- \leftrightarrows S^{32}O_2 + HS^{34}O_3^-$				(Exp. 1.019 25°C)		
30	$S^{34}O_2 + HS^{32}O_3^- \leftrightarrows S^{32}O_2 + HS^{34}O_3^-$				(Exp. 1.043 25°C)		
31	$HS^{32}O_3^-$ (sol.) $+ S^{34}O_2(g) \leftrightarrows HS^{34}O_3^-$ (sol.) $+ S^{32}O_2(g)$					1.019	
32	$HS^{32}O_3^-$ (sol.) $+ S^{34}O_2(g) \leftrightarrows HS^{34}O_3^-$ (sol.) $+ S^{32}O(g)$					1.039	
33	$HD + H_2O(l) \leftrightarrows HDO(l) + H_2$				Exp. 3.2		1.28[1]
					Calc. 3.81		1.36[1]
34	$HT + H_2O \leftrightarrows HTO + H_2$			Exp.	7.74	6.26	2.08
				Calc.	7.64	6.19	1.99
35	$HD + H_2O(g) \leftrightarrows HDO(g) + H_2$	4.19	3.62	2.43[2]			
36	$HDO(l) + D_2 \leftrightarrows D_2O(l) + HD$	3.96	3.33	2.21[2]			
37	$NH_3 + NHD_2 \leftrightarrows 2\ NH_2D$	2.92	2.94	3.00[3]			
38	$NH_2D + ND_3 \leftrightarrows 2\ NHD_2$	2.88	2.90	2.99[4]			
39	$NH_3 + HD \leftrightarrows NH_2D + H_2$	6.85	5.83	2.07[5]		3.59	2.06[5]
40	$NHD_2 + D_2 \leftrightarrows ND_3 + HD$	2.59	2.23	0.87[5]			
41	$NH_3 + HDO \leftrightarrows NH_2D + H_2O$	1.64	1.61	1.49[4]			
42	$NHD_2 + D_2O \leftrightarrows ND_3 + HDO$	0.732	0.719	0.663[5]			
43	$SiO_2^{16} + H_2O^{18} \leftrightarrows SiO^{16}O^{18} + H_2O^{16}$	1.030[7]		1.014[8]			
44	$Si^{28}F_4 + Si^{30}F_4 \leftrightarrows Si^{30}F_4 + Si^{28}F_4$		1.002				
45	$Sn^{120}Cl_4 + Sn^{116}Cl_4 \leftrightarrows Sn^{116}Cl_4 + Sn^{120}Cl_4$		1.00025				

TABLE 37.—*Continued*

No.	Reaction	Equilibrium Constants (K)			Enrichment Factors (α)		
		0°C	25°C	327°C	0°C	25°C	327°C
46	$Cl_2^{37} + Cl^{35}O_3^- \leftrightarrows Cl_2^{35} + Cl^{37}O_3^-$		1.024				
47	$Cl_2^{37} + Cl^{35}O_3^- \leftrightarrows Cl_2^{35} + Cl^{37}O_3^-$		1.040				
48	$Cl_2^{37} + Cl^{35}O_4^- \leftrightarrows Cl_2^{35} + Cl^{37}O_4^-$		1.077				
49	$S^{32}O_4^- + H_2S^{34} \leftrightarrows S^{34}O_4^- + H_2S^{32}$		1.075				
50	$H_2S^{34} + S^{32} \leftrightarrows H_2S^{32} + S^{34}$		1.000				
51	H_2S^{32} (g) + HS^{34-} (sol.) $\leftrightarrows$ H_2S^{34} (g) + HS^{32-} (sol.)		1.006				
52	H_2S^{32} (g) + $S^{34=}$ (sol.) $\leftrightarrows$ H_2S^{34}(g) + $S^{32=}$ (sol.)		1.013				

[1] 527°C.
[2] 127°.
[3] 300°C to ∞.
[4] 400–500°C.
[5] 500°C.
[6] 182°C.
[7] 15°C.
[8] 203°C; given as 140°C by Silverman. *See* page 337 for explanation of correction.

Equations 5, 18, 24, 25, 27–30, 33, 34 from Urey (1947, p. 575); 31, 32 from Thode et al. (1949, p. 369); 35–42 from Kirshenbaum (1951, p. 53–58); 43 from Silverman (1951, p. 30); 44, 45 from Bigeleisen and Mayer (1947, p. 267); 46–48 from Clewett (1950, p. 12); 49–52 from Tudge and Thode (1950, p. 575–577); all others from Urey and Greiff (1935, p. 325).

Abbreviations used in table:
(l) liquid
(g) gas
(sol.) solution
(amal.) amalgam
(aq.) aqueous
(Exp.) experimental
(Calc.) calculated

29–32 have been used by Thode and his coworkers (1945; 1949) in predicting and demonstrating natural fractionation of the isotopes of sulfur. Silverman (1951, p. 30) has used (43) in establishing a tentative isotopic temperature scale for determining temperatures of formation of silica.

The other equations can be used, either directly or by analogy, to predict expected isotopic fractionation by natural processes involving exchange reactions at equilibrium. For example, (45) indicates that if tin is brought into pneumatolylic deposits as a halide no detectable fractionation would be expected, even between Sn^{124} and Sn^{112} for which $K \sim 1.0015$. Equation (26), on the other hand, suggests that nitrates fixed by lightning should be measurably enriched in N^{14} with respect to free nitrogen of the atmosphere if the temperature of reaction is not too high. *See* section on Biologic Processes for further discussion of this problem.

Likewise, ammonium sublimates around volcanoes should be significantly enriched in N^{15} with respect to free ammonia of the volcanic emanations (27).

Constants for many more equilibria of this type should be worked out as guides for experimental work in the geology of stable isotopes. For maximum usefulness these equilibria should:

(1) Represent reactions that are probably operative (or at least approximated) in natural processes.

(2) Involve isotope pairs that have (a) a mass ratio that makes fractionation probable, and (b) an abundance ratio that allows ready and

accurate determination of the isotopes. (*See* below for suggestions of such isotope pairs.)

(3) Cover the probable temperature ranges of the natural reactions.

Four important problems to which this approach should be applied are:

(1) Revision of the quartz isotope thermometer and its extension to the other forms of silica.

(2) Development of a similar temperature scale for feldspars, tourmaline, and other pegmatite and vein silicates. Many of those minerals, as well as quartz, can now be grown in the laboratory under controlled conditions, so these temperature scales could be placed on a firmer basis than those upon which current methods of estimating temperatures of formation of these minerals rest, at least for the temperature range where significant fractionation takes place.

(3) Sulfides would no doubt be much more difficult to handle experimentally. Even with little or no experimental work, a calculated temperature scale of this kind for a few important ore-related sulfides (FeS_2, PbS, ZnS, $CuFeS_2$, etc.) would probably provide a better method of estimating temperatures than is currently available.

The importance of these determinations in economic geology, geochemistry, and other theoretical geologic studies of pegmatites and veins is obvious. They would apply equally well, or perhaps even better, to such questions, as the origin of (supposed) authigenic quartz, feldspar, and tourmaline and the manner of formation of certain types of deposits in sedimentary rocks that have been interpretated as syngenetic.

(4) Extension of the calcite isotope thermometer to include the isotopes of calcium, Ca^{42} and Ca^{46}, to check the values obtained using O^{16} and O^{18}, and then the relations between calcite and dolomite, and an independent temperature scale for dolomite. This would almost certainly make possible positive distinctions between hydrothermal dolomite on the one hand and primary sedimentary and low-temperature-replacement dolomite on the other and might even distinguish between the latter two.

Base Exchange and Adsorption

Migration of ground water and possible changes of its isotopic composition by travelling long distances through aquifers are discussed in the section on Diffusion. It is pointed out there that base exchange and adsorption may modify or obscure any effect due to differential migration of molecules of different masses.

There is definite experimental evidence that base exchange strongly predominates over any effect of diffusion or similar processes when solutions of appropriate ions percolate through zeolites. (*See* sections on Lithium and Potassium in Part I.) The same thing is no doubt true for clays that have base-exchange capacity and may also apply to adsorption on very finely divided minerals, such as fresh feldspar and quartz, which have little or no ability to undergo base exchange.

These base-exchange reactions are not analogous to the exchange equilibria in Table 37, although one such reaction (No. 24) is given. There is no basis now for predicting the magnitude, or even the sign, of the constants for these reactions. (Note that for Equation 24 the value of α was determined experimentally, not calculated.)

For example, the isotopes of lithium and potassium behave oppositely in base-exchange reactions with (sodium) zeolites:

$$Li^7Z + Li^6 \rightleftarrows Li^6Z + Li^7; \qquad \alpha > 1$$

but

$$K^{41}Z + K^{39} \rightleftarrows K^{39}Z + K^{41}; \qquad \alpha < 1$$

which shows that the lighter lithium isotope is picked up more readily and held more tightly by the zeolite than the heavier ones, whereas the heavier isotope of potassium is preferred by the zeolite. These relations would not have been predicted by current theory; each situation of this kind must be evaluated experimentally, so there are exciting possibilities of finding isotopic fractionations that have been produced in this manner and of making secure interpretations on the basis of them. Efficient separations of rare earths with closely similar atomic weights and chemical properties and of isotopes of other elements have been made in the laboratory by similar reactions involving resins and artificial zeolites. This subject is discussed exhaustively in a series of papers that appeared

in the Journal of the American Chemical Society for November, 1947 (Bauman and Eichhorn, 1947; Boyd *et al.*, 1947; Marinsky *et al.*, 1947; Spedding *et al.*, 1947; and Tompkins *et al.*, 1947). These articles give many references to earlier work.

On the basis of these considerations, significant isotopic fractionation of lithium, potassium, and similar elements would be expected in aquifers containing appreciable quantities of zeolites, base-exchangeable clays, and possibly just finely divided minerals that do not undergo base exchange.

Problems of ground water that could be attacked by studying isotopic fractionation produced by base exchange and adsorption are of the same types mentioned in the section on Diffusion. For example, direction and distance of migration might be determined. By studying also migration between wells and contents of C^{14} and/or H^3 better answers might be obtained to problems of velocities of flow and of age of the ground water.

Near-surface ground water could be studied in the same manner except that age determinations would be meaningless because the water would be in equilibrium with atmospheric CO_2. The other interpretations would be less positive than those made on extensive buried aquifers and would have to be made carefully with reference to local conditions.

Dissolved salts in ore-forming solutions would probably be subject to the same type of fractionation in moving along a fault (or fault zone), in contact with gouge, or in percolating through sedimentary rocks or other porous materials. Isotopic analyses of the alkali- and alkaline-earth metals from the minerals of a vein, from the liquid inclusions in the vein minerals, and from the country rock near the vein (samples spread as widely as possible) might develop a pattern that would show very definitely the direction of motion of the solutions that gave rise to the deposit. Temperature pattern at the time of formation and other complicating factors would have to be eliminated, or evaluated carefully. For example, effect of temperature could be eliminated by considering only a portion of a deposit that was formed essentially at one temperature; it could be evaluated by applying corrections for differences in temperature where the temperature coefficient is large enough to warrant doing so.

Biological Processes of Separation of Isotopes

Known Examples

Biological processes of separation of isotopes are, of course, merely physical and/or chemical processes operating in an organism. They appear, in many cases, to be more efficient than similar processes in inorganic nature. Moreover, they offer compact examples readily discussed as biological processes, which would be difficult to classify with certainty as due primarily to a certain physical or chemical process.

Kamen (1946, p. 124–125) summarizes the examples of density determinations of water from plants and concludes that there is good evidence of a relation between density and rate of evaporation; there is probably fractionation by diffusion through and out of the plant tissues. Increases in density up to about 4 γ have been observed. The evidence is less convincing for water from animal tissues, but increases up to about 2.5 γ have been measured.

Higher C^{12}/C^{13} ratios for organic carbon than for inorganic are generally accepted. (*See* section on Carbon), but the mechanism of concentration of the C^{12} is not so well understood as is the concentration of heavy water in plants. The concentration of K^{39} in certain types of plants has been postulated (*e.g.*, Brewer, 1938a) but is not well established, either as to amount or mechanism (Cook, 1943, p. 293).

Other Typical Problems

A. *Origin of arkose.*—There is long-standing disagreement whether arkose is the product of slow weathering in an arid climate or rapid weathering in a tropical humid climate. Perhaps some is formed each way; in any case a method of making clean-cut distinctions would be of considerable interest.

Wickman (1952, p. 252) made a number of C^{12}/C^{13} determinations on plants from tropical rain forests and several from deserts. All the desert plants gave a value of 89.6; those from humid tropical regions showed a strong maximum at 91.1, with no values below 90.7. If

this distinction is as positive and universal as appears probable from Wickman's results, then a good C^{12}/C^{13} determination on plant remains or carbonaceous material in or closely associated with an arkose (in shaly layers) should provide an unequivocal answer concerning the type of conditions under which it was formed.

B. *Origin of nitrate deposits.*—There have been extended arguments over the organic or inorganic origin of nitrate deposits like those of northern Chile. If it can be established that organic nitrogen has a characteristic value or range of values for N^{14}/N^{15}, different from that of inorganic nitrogen, then determinations of N^{14}/N^{15} for the nitrate deposits should provide information worth while in making interpretations of origin.

C. *The selenium cycle; abundance of selenium.*—The mass ratio Se^{82}/Se^{76} is 1.079. This value is intermediate between those for S^{34}/S^{32} (1.062) and C^{13}/C^{12} (1.083), for both of which significant natural fractionations have been reported. Similar fractionation might be expected for Se^{82}/Se^{76} even by inorganic processes. It is well known that some plants take up selenium in a highly preferential manner (Trelease and Beath, 1949, p. 121–122). In western North America these plants commonly grow in a semiarid environment where evaporation, and consequently transpiration, are rapid. All these factors are favorable for isotopic fractionation of selenium.

Determinations of Se^{82}/Se^{76} for a variety of materials—primary sulfides and selenides, oxidized zones of seleniferous deposits, soils, volcanic ash, and other selenium-bearing formations, surface and ground water in and near selenium-rich areas, and plants in many different situations—should prove to be very interesting. If values of the ratio fall into a few well-defined groups, say (1) primary, (2) chemically transported, and (3) organic, then it would be possible, on the basis of relatively few isotopic analyses, to say that a given formation (ash bed) probably contains primary selenium. This would not only have the practical value of a warning not to grow food or forage anywhere on the outcrops of that formation, but also would be a useful aid in calculating the abundance of selenium; such a formation should have a more or less uniform selenium content, except on weathered outcrops, whereas a formation to which selenium had been added by percolating waters should show highly variable selenium content.

The results might also suggest mechanisms of solution, transport, deposition, utilization by plants, etc., that would aid in a more detailed description of the selenium cycle.

D. *Source of minor elements in phosphate deposits.*—Several heavy metals occur in the Northwest phosphate deposits in quantities that might, under favorable circumstances, be extracted as by-products. Knowledge of where these metals came from and how they were incorporated in the deposits might aid in exploiting them. At least four of them, Cr, Mo, Ni, and Zn, have isotope pairs for which mass ratios are such that some natural fractionation is not out of the question. Careful isotope determinations on these elements from the deposits, from plants, and from other sources might shed some light on the source of these metals in phosphate deposits.

E. *Origin of thucolite.*—Determinations of C^{12}/C^{13} ratios for thucolite and similar uranium minerals could probably indicate whether the carbon was primary—*i.e.*, derived from a magma via hydrothermal solutions—or whether it represents reworked organic material. On the answer to that question could hinge theories of origin of uranium deposits like those of the Rand and the Colorado Plateau. The answer could thus have a great effect on the philosophy and techniques of prospecting such deposits.

Changes in Isotopic Abundance by Natural Fission

Natural fission of U^{235} has not yet been proved.[14] Studies of isotopic composition of some of the minor elements in pegmatites containing uranium minerals and in other pegmatites without such minerals offer a possibility of demonstrating it.

Siegel (1946, p. 2437) gives a graph showing the per cent yield of the various fission products

[14] Mark Inghram (personal communication) has recently measured the isotopic composition of Xe and Kr from a uranium mineral. He finds the isotopes present in nowhere near normal abundance The amounts are consistent with production of at least part of these gases by nuclear fission. Thus it appears that the fact of natural fission of U^{235} has been established, but it has not been evaluated quantitatively.

of U^{235} plotted against their mass numbers. There are two fairly sharp maxima on the curve: (1) elements with mass numbers 89–103; Y, Zr, Nb, Mo, Ru, Rh, and Pd are present in amounts in excess of 3% each; (2) elements with mass numbers 131–147; Xe, Cs, Ba, La, Ce, Pr, Nd, and Sa are present in amounts in excess of 2% each. If current theories of the origin of nuclear species are correct there is no reason to expect that isotopic abundances among the fission products will be like those of the corresponding elements in the earth's crust. In fact, there is every reason to believe that the distribution pattern will be quite different.

The half lives of the radioactive fission products are so short that only the stable end products need be considered in such a problem. If a significant amount of natural fission has occurred, say in a very old pegmatite containing important amounts of uranium minerals, then the isotopic composition of the elements mentioned (Y to Pd and Xe to Sa) should differ by a measurable amount from the values for the same elements in a pegmatite with no uranium minerals.

It should be pointed out that mass ratio does not enter the picture because the question is not one of isotope separation, but of adding material with an abnormal ratio.

If any considerable amount of natural fission can be detected it will be necessary to revise estimates of the amount of heat contributed to the earth by disintegration of uranium, as well as of the original ratio of U^{235} to U^{238}.

Stratigraphic Correlation

Where conventional criteria for making stratigraphic correlations are missing it is possible that comparing isotope ratios of the strata might help. This might be done on carbonates, quartz, suites of heavy minerals, or other minerals or combinations, depending on the specific problem.

Miscellaneous Problems; Other Isotope Pairs

U^{238}/U^{235}

As indicated, all determinations of the ratio U^{238}/U^{235} have given the same value, within experimental error. However, there are valid grounds for pursuing the matter further. Most of the determinations have been made on the same general type of material and so would not be expected to show differences. Samples from as many localities and from as widely divergent types of deposits as possible should be analyzed. Although the chances of finding significant variations in minerals are very slight indeed, the great advantages of having a source richer in U^{235} would justify some further work on the problem. With greater U^{235} content, ores of lower over-all uranium content could be worked.

There would be a greater chance of finding measurable differences in the uranium taken up by plants. Helen Cannon (unpublished U. S. Geological Survey reports) has found that some of the "selenium selector" plants also take up uranium to a greater extent than would be predicted on the basis of the uranium content of the soils in which they grow. Uranium from those plants should be studied isotopically.

Further work is also justified on this problem from the point of view of theoretical isotope geology. The mass ratio U^{238}/U^{235} (1.013) is very low (although not as low as for some pairs of isotopes of lighter elements; *e.g.* Sn^{120}/S^{119} = 1.0084) and the molecular weights of uranium compounds are very high, so no detectable fractionation is to be expected. If fractionation should be demonstrated, then separation of almost *any* pair of isotopes in nature could be anticipated. On the other hand, if no natural separation can be found, the next step is to return to elements of lower atomic weights and higher mass ratios of isotope pairs and work up the periodic table until natural separation becomes insignificant.

However, there will probably be no sharp line below which fractionation is effective and above which it is not. Elements with higher atomic weights may have a greater spread of isotopic masses and thus be able to show some natural separation of isotopes where their lighter neighbors cannot. There would be expected, then, a zone (probably below the mid-point of the atomic-weight scale) in the periodic table within which some elements will undergo natural fractionation of isotopes and some will not, but above which no element will show frac-

tionation detectable by present methods of measurement.

Other Possibilities

Numerous problems are suggested above involving isotope pairs that have already been shown to fractionate naturally, and some that have not. There is no point in picking out numerous other possibilities; they can be selected easily from any table of isotopic weights and abundances. The types of problems to be undertaken have been stressed, and these same types can be tried with numerous other elements that could be chosen.

There are, however, two such pairs, Cl^{35}/Cl^{37} and Ca^{42}/Ca^{43}, for which some problems have already been outlined above that are worth emphasizing just now because: (1) their isotopic constants are favorable, (2) in atomic weights they are just above the heaviest element for which natural fraction has been positively demonstrated (sulfur), and (3) they are so widespread in occurrence that if fractionation is demonstrated for them they can probably be used in most of the types of problems outlined above: geologic thermometry, movement of solutions, organic or inorganic origin of materials (especially for Ca), chemical fractionation in various kinds of reactions, as well as the specific problems mentioned above for these elements.

CONCLUSION

Study of the distribution of the nonradiogenic isotopes of elements is a powerful new tool of geologic research. It has already provided independent checks for interpretations that have been made by other methods, and has made possible new interpretations. More and more fields are bound to open rapidly for this new approach to geologic and related problems; the new ones suggested above, even if they were all worked out, would constitute just the beginning of what this method should accomplish.

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Short Notes

POSSIBLE DEEP-SEA TURBIDITY-CURRENT CHANNELS IN THE INDIAN OCEAN

BY ROBERT S. DIETZ

In 1948, the steamship ALBATROSS of the Swedish Deep Sea Expedition obtained an echogram across the eastern Indian Ocean while enroute to Ceylon along the track shown in Figure 1. The Kelvin-Hughes echo sounder was operated part of the time on the "normal scale" which gives only a small-scale presentation of the bottom topography, resolving only the gross topography, and part of the time on an "enlarged scale", which gives a "blown-up" portrayal of the bottom. Frequent use of the enlarged scale (in which the paper width of about 7 inches represents 150 fathoms and the paper speed is about 15 inches per hour) showed that the sea floor in this region was extremely smooth except for the occasional trough-shaped depressions of the bottom (Pl. 1).

The writer was first shown these interesting features, along with other portions of the ALBATROSS echograms, by Dr. Fritz Koczi and Dr. Hans Pettersson at the Brussels meeting of the International Union of Geodesy and Geophysics. It was suggested that these depressions might be some type of tectonic feature such as a small graben. It was the view of Doctor Pettersson, leader of the Swedish Deep Sea Expedition, that the smooth bottom in this part of the Indian Ocean might be related to an extensive lava flow. In support of this interpretation, it was pointed out that the bottom seemed hard since the piston corer was broken at Station 209, and difficulty was encountered in coring at Station 210. The echogram shows little variation from a level plain over the area scanned between successive "pings". It seemed unlikely to the writer that a lava flow would be this smooth, whereas a sedimentation plain might have such smoothness. It appeared more likely that these depressions might be profiles across deep-sea channels formed by turbidity currents. A recent more detailed study of a microfilm copy of the ALBATROSS echogram has given him sufficient conviction of this point of view to publish this short note. The writer wishes to express his thanks to Doctors Koczi and Pettersson for permission to utilize portions of the ALBATROSS echogram to publish this interpretation.

For convenience, the depressions are termed here Able, Baker, Charlie, Dog, and Easy—thus using the phonetic alphabet. Able is located in the central part of the eastern Indian Ocean about 400 nautical miles southeast of Ceylon, whereas Baker, Charlie, Dog, and Easy are located in a group about 120 nautical miles southeast of Ceylon. Able is especially remarkable. It is more than 4 miles across at the top, it has a depth of 240 feet, and the sides are raised 90 feet higher than the surrounding sea floor. In the center a mound is present. Baker, Charlie, Dog, and Easy are almost a mile across and have depth, respectively, of 60, 180, 240, and 30 feet. The bilateral symmetry of all of the depressions is striking. Of the ten sides shown, only the east side of Charlie is not raised.

Leveed banks seem to be typical of the deep-sea channels which are extensions of submarine canyons off California, suggesting that these Indian Ocean depressions may be channels. Such levees were first noted to be typical of the channel extension of La Jolla canyon across the gently sloping bottom of San Diego Trough (Menard and Ludwick, 1951). Buffington

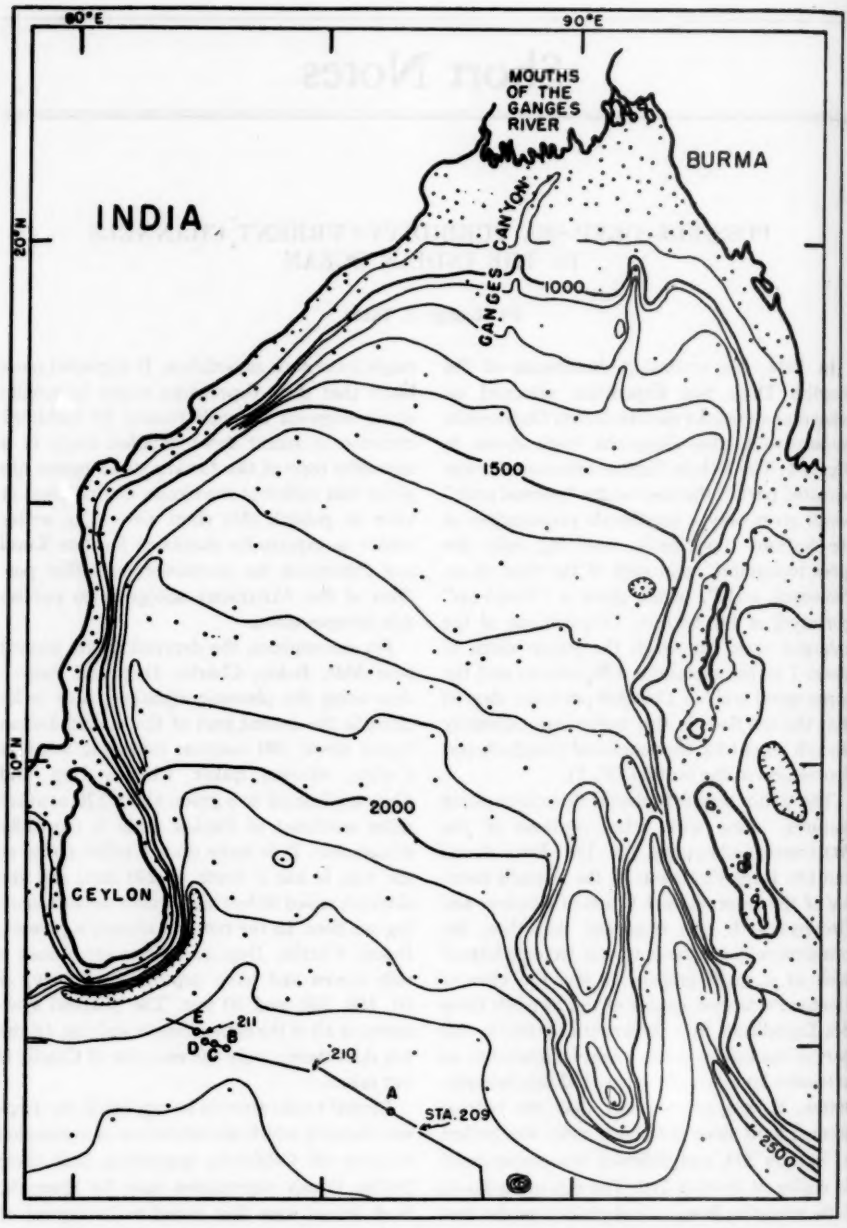
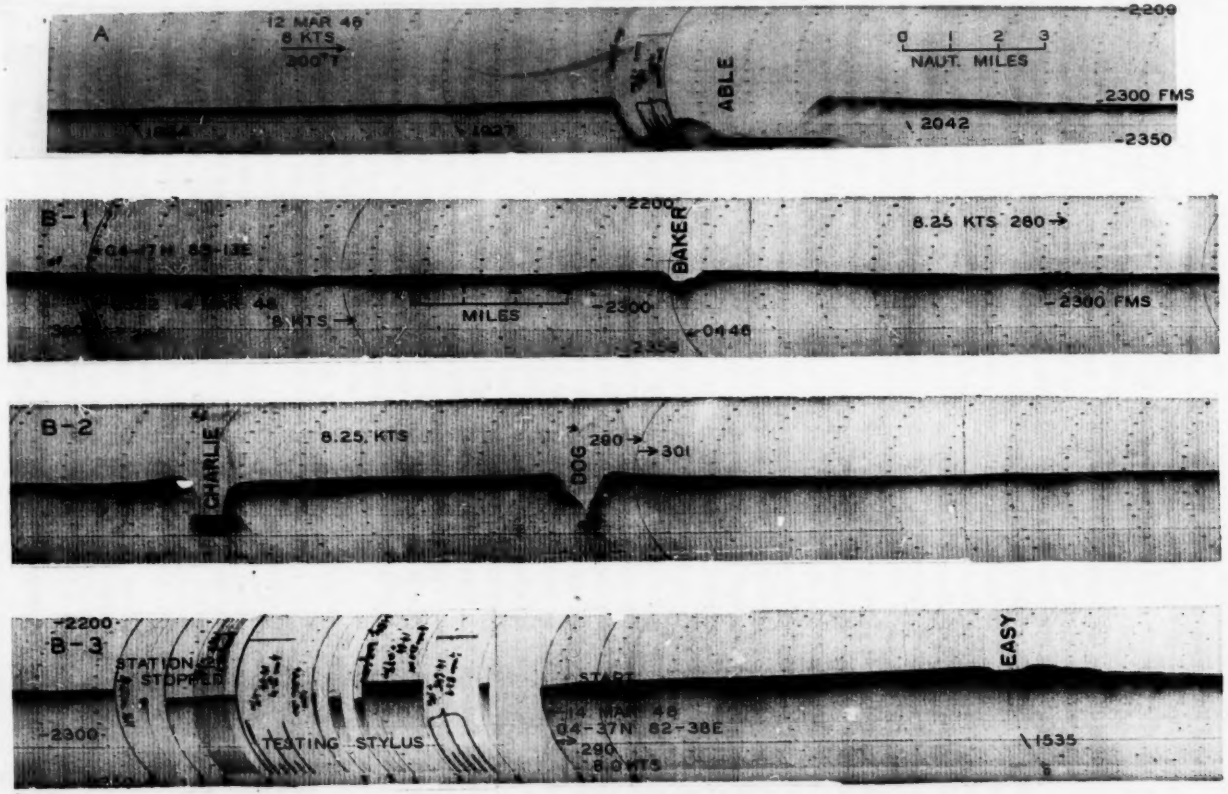


FIGURE 1.—CHART OF THE WESTERN ARM OF THE INDIAN OCEAN (the Bay of Bengal)

Showing the bathymetry based on soundings shown on Hydrographic Office chart no. 5445. The positions of the soundings are shown by dots. The track of the ALBATROSS is shown along the bottom of the chart, and the positions of the presumed deep-sea channels are shown by circles along this track.



ECHOGRAM SHOWING PRESUMED DEEP-SEA CHANNELS DISCOVERED BY THE ALBATROSS

Vertical exaggeration is about 20 times.

(1952) has described many leveed subsea channels off the west coast. Dill, Dietz, and Stewart (unpublished manuscript) have reported that portions of the deep-sea channel extension of the Monterey submarine canyon show levees. Recently the USS EPCE(R) 857 of the Navy Electronics Laboratory recorded four deep-sea channel-like crossings with an Edo echo sounder off northern California and Oregon. One channel was traced for about 200 miles and, on some crossings, was leveed. However, Ericson, Ewing, and Heezen (1951) do not report levees from the deep-sea channel extending out from the Hudson submarine canyon. Thus, levees do not invariably accompany deep-sea channels but seem to be commonly associated with them.

The raised sides of these Indian Ocean depressions do not preclude the possibility of their being tectonic features, but, in the writer's opinion, the most logical explanation is that they are deep-sea channels formed by turbidity currents flowing out from the Bay of Bengal. The low gradient of the raised sides and the symmetry in profile of the depressions seem to preclude their formation by mud flows or by turbidity currents of high density. Slowly flowing, low-density turbidity currents of great volume and nicely adjusted to the gradient of the bottom appear to be required. Such currents must more than fill the channel so that eddies, too small to continue on as independent turbidity flows, are sluffed off. These must mix with the surrounding bottom water and slowly drop their load of suspended particles. As noted above, Charlie lacks a "levee" on one bank. The other bank has an unusually well-developed "levee." Is it not possible that this well-developed "levee" formed on the outside of a turn in a channel where any overflow would take place over the outside bank?

It may appear to some readers that turbidity currents have been too widely invoked as a sea-floor process in the past few years. It is well known, however, that a very slight increase of salinity or a decrease of temperature of a water mass with respect to the surrounding water will cause it to underflow the surrounding water, if the mass of water with increased density is large. Bell (1947) showed that an increase in the volume of stream-fed cold water entering Shaver Lake greatly reduced mixing. If there is sufficient internal turbulence to prevent the settling-out of particles, it is reasonable to expect that a mass of water with its density increased because of sediment will behave in a manner similar to one with its density increased because of temperature or salinity. It is possible that these water masses which are presumed to flow in these channels are in part impelled by, and possibly initiated by, a water mass with low temperature and/or high salinity, but sediment must be a contributing factor in order to account for the build-up of the leveed banks.

In Figure 1 it can be seen that the topography of the Bay of Bengal is extremely simple. It has the form of a smooth southward-sloping plain with a gradient of about 1 fathom per mile. This simplicity of shape suggests that the sea floor here has been tectonically stable for a long period of time and that the initial tectonic irregularities have been largely masked by sedimentation. The uniform gradient suggests that this gradient is determined by the profile of equilibrium of some sea-floor process. Could not this process be turbidity currents? If so, one would expect a north-south system of channels to be present throughout the entire Bay of Bengal. Is it not even possible that Able is a channel continuing northward, normal to the regional slope, and eventually tying into the mouth of the enormous Ganges submarine canyon 1100 nautical miles away? This possibility is made more plausible when one considers that Able is about eight times as wide and five times as deep as the Mississippi is (below its raised sides) in the vicinity of New Orleans.

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NEL PROFESSIONAL CONTRIBUTION NO. 10

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DETERMINATION OF THE AGE OF LEPIDOLITES BY THE METHOD OF ISOTOPE DILUTION

By G. L. Davis and L. T. Aldrich

Since 1945 many elements of the periodic table have been available with isotopic abundances different from those in naturally occurring sources. This had made possible the measurement of trace quantities of these elements in minerals by the method of isotope dilution

Table 1.—Abundance Measurements for Standardization of "Spike" Solution of Sr

Source	Isotope			
	88	87	86	84
Normal Sr	.825	.070	.099	.006
Spike Sr	.213	.032	.119	.636
Mixture: 201 μg normal and 10.0 ml "spike" Sr	.702	.063	.103	.129

(Inghram, Brown, Patterson, and Hess, 1950; Tilton, Patterson, and Inghram, 1952). We have applied this technique to the determination of Rb^{87} and Sr^{87} in lepidolites and have thereby determined the relative age of a number of pegmatites.

Ahrens and coworkers (1949; 1950; 1951) have obtained the ages of many lepidolites by spectrochemical analysis. This method of analysis could give valid results only in the favorable case of lepidolite where at least 99 per cent of the Sr is radiogenic (Mattauch, 1937). Analysis of lepidolite by isotope dilution provides an independent determination of mineral age. It also provides a sensitive indication of any contamination occurring in this analytical procedure.

The first step in the determination of Sr by isotope dilution is the standardization of the "spike," a solution of Sr of abnormal isotopic abundance obtained from the Atomic Energy Commission. Table 1 shows typical abundance values based on mass-spectrometric measurements.

From the values given the standardization of the spike solution may be completed from the equation

$$X = Ak \frac{.825\left(\frac{.129}{.702}\right) - .006}{.636 - .213\left(\frac{.129}{.702}\right)}$$

where

X = micrograms Sr/10 ml in the spike
A = micrograms normal Sr in the mixture
k = correction factor due to the different atomic weights of normal and spike Sr.

Similar measurements and calculations are required for standardizing the Rb spike solution.

Table 2.—Abundance-Ratio Measurements for the Determination of Sr^{87} of Radiogenic Origin in Lepidolite from Pala, California

Source	Ratio	
	88/84	87/84
Spike	.335	.050
3.00 g lepid. + 49.0 μg spike	.338	.612

Table 2 shows the mass-spectrometer determinations of the isotopic abundance ratios for the spiked lepidolite sample and for the spike. The difference between the 88/84 ratios measures the amount of ordinary Sr present in the mineral and introduced in processing. In this case the contamination by ordinary Sr is negligible. The determination of the radiogenic Sr^{87} is simply the difference between the 87/84 ratios multiplied by the micrograms of Sr^{84} in the spike.

It is our experience that radiogenic Sr may be determined in minerals in which the ratio of ordinary Sr to radiogenic is of the order of 20. Such minerals are biotite and the potassium

feldspars. The determination of the Rb content of the sample is obtained by the same kind of measurements.

TABLE 3.—Rb AND Sr DETERMINATIONS AND DERIVED AGES OF FOUR LEPIDOLITES

Location	Rb^{87} (mg/gr)	Sr^{87} (μg/gr)	Age in millions of years
Pala, California	4.12 ±.04	6.05 ±.10	147 ±5
Black Hills, South Dakota	3.38 ±.04	67.7 ±1.0	2000 ±20
Winnipeg River, Manitoba	7.15 ±.07	260 ±3	3360 ±100
Bikita Quarry, S. Rhodesia	8.75 ±.10	300 ±5	3160 ±100

Table 3 lists measurements on four specimens of lepidolite. The ages shown are based on the value of the Rb^{87} decay constant of 1.08×10^{-11} yr^{-1} (MacGregor and Wiendenback, 1952). This decay constant is 10 per cent lower than that used by Ahrens (1949) and thus does not explain the substantial differences between our age measurements and those previously determined, particularly for the lepidolites from Winnipeg River and Salisbury.

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